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SOIL SCIENCE

VOLUME 70

JULY TO DECEMBER, 1950

RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY
U. S. A.

PUBLISHED BY
THE WILLIAMS & WILKINS COMPANY
BALTIMORE, MARYLAND

SOIL SCIENCE

Founded 1916 by Jacob G. Lipman

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Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879

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SULFUR SYMPOSIUM

This issue of SOIL SCIENCE is entirely devoted to a series of papers on sulfur that were presented before the Division of Fertilizer Chemistry of the American Chemical Society at its annual fall meeting held in the Convention Hall at Atlantic City, New Jersey, on Tuesday, September 20, 1949. The meeting was attended by some 200 chemists who were interested in knowing more about sulfur relationships in soils, microorganisms, and crop plants and the extent to which sulfur may have value as a constituent of fertilizers. These papers present a fairly complete picture of our knowledge of this element in relation to agriculture. We are pleased to publish them for the benefit of the readers of the Journal.

FIRMAN E. BEAR

SULFUR IN THE AMERICAN FERTILIZER INDUSTRY

VINCENT SAUCHELLI[1]

The Davison Chemical Corporation, Baltimore

Sulfur occupies a pre-eminent place in agriculture: it is an indispensable plant nutrient; a valuable fungicide; and a chemical raw material necessary in the manufacture of the largest world-wide single commercial fertilizer—superphosphate- and such other plant-nutrient carriers as the sulfates of ammonia, potash, calcium, copper, manganese, zinc, magnesium, and cobalt. For more than a century, sulfur-containing fertilizers have been increasingly used in agriculture; the history of the sulfur industry therefore parallels that of commercial plant food. Agriculture is the largest consumer of sulfur; in fact, consumption of sulfur by agriculture reflects the economic position of the farm community. Industry consumes sulfur in the form of sulfuric acid and not as the element. Approximately one third of the total production of sulfuric acid in this country—about 3.5 million tons (100 per cent basis)—is used in the manufacture of commercial fertilizers.

HISTORICAL REVIEW

Early in the 19th century Justus von Liebig in Germany was able to prove, on the basis of careful studies, that plant life feeds on mineral substances and not, as was held by many up to that time, upon the organic material of manure and similar matter in the soil. He further showed that phosphorus from bones would be more quickly accessible to plant roots if the bones were first treated with sulfuric acid. This discovery led Sir John Lawes in England to treat mineral phosphates, such as coprolites, with sulfuric acid. He succeeded in getting similarly favorable results on plant growth with these acid-treated mineral phosphates. By commercializing this knowledge, Lawes laid the foundation of today's vast rock phosphate-superphosphate world industry. The growth of this industry was given impetus by the discovery of high-grade rock phosphates in South Carolina shortly after the Civil War, and it continued its remarkable

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[1] The author is indebted to Robert Frank of Chemical Construction Corporation, New York, and to T. R. Harvey of Monsanto Chemical Company, St. Louis, for many helpful suggestions.

TABLE 1

*Location of sulfuric acid plants in the United States**

STATE	1939		1946	
	Contact	Chamber	Contact	Chamber
Alabama	2	6	2	6
Arizona	1	1	2	1
California	6	—	8	—
Colorado	1	—	1	—
Connecticut	1	1	1	1
Delaware	1	—	1	—
Florida	1	3	2	5
Georgia	—	13	—	15
Illinois	5	5	7	6
Indiana	3	1	3	1
Kentucky	1	—	1	0
Louisiana	2	3	3	3
Maine	—	—	1	—
Maryland	2	5	2	6
Massachusetts	1	1	1	1
Michigan	1	2	2	2
Mississippi	—	3	—	3
Missouri	2	—	2	—
Montana	—	1	—	1
New Jersey	6	5	7	5
New York	2	2	2	1
North Carolina	—	8	1	8
Ohio	5	9	6	9
Oklahoma	2	—	2	—
Pennsylvania	10	6	10	5
Rhode Island	1	—	1	—
South Carolina	—	8	—	8
Tennessee	1	4	1	3
Texas	4	1	7	1
Utah	1	—	1	—
Virginia	3	—	4	6
Washington	1	6	1	—
West Virginia	1	—	1	—
Wisconsin	2	1	1	—
Wyoming	1	—	1	—
Total	70	95	85	97

* Source: U. S. Domestic Commerce.

development with successive discoveries of rock phosphate deposits in Florida, Tennessee, the Pacific Islands, North Africa, and the Rocky Mountains. In 1947, the world produced about 19 million tons of superphosphate (20 per cent basis), of which the United States produced more than 9 million tons.

To convert rock phosphate to 18 to 20 per cent superphosphate requires approximately equal weights of the finely ground rock and 50° Bé sulfuric acid. The process is economical and efficient and for more than a century has been able to hold its predominant position in the trade against all competitors. Thus fertilizer practices have linked sulfur and phosphates in a close bond throughout this long period.

To make sulfuric acid it is necessary to convert the sulfur to sulfur dioxide, further oxidize it to sulfur trioxide in the presence of a catalyst, and then cause the trioxide to react with water. The process itself is relatively simple. Sulfur for this purpose is derived either from brimstone or from a sulfide, such as iron sulfide or pyrite. Sulfuric acid has become the leader of the chemical industry because it is a relatively low cost commodity and enters so many chemical processes. In the search, discovery, and development of present supplies of brimstone, great men have written one of the most thrilling chapters in our amazing modern chemical industry—a chapter filled with all the hopes, courage, resourcefulness, and triumph against tremendous odds that are so characteristic of all great human adventure. In this history we see the struggle of ambitious, greedy men to monopolize and exploit a natural resource for self-gain thwarted by the skill and ingenuity of other men who, by developing new technologies, succeeded in smashing that monopoly.

TABLE 2

*Growth of sulfuric acid plants in the United States, 1915–1946**

YEAR	CHAMBER	CONTACT
1915	175	15
1920	178	27
1925	152	37
1930	126	46
1935	71	63
1940	96	74
1941	97	78
1942	99	82
1943	100	86
1944	101	90
1945	99	87
1946	97	85

* Source: Based on Chemical Engineering and Chemical and Metallurgical Engineering statistics.

In the early industrial period 1865 to 1890, more than half of the sulfuric acid consumed in this country was derived chiefly from Sicilian brimstone. In succeeding years new processes were developed, utilizing sulfur from pyrites, so that from 1890 to 1915 pyrites gradually, through lower prices, supplanted brimstone. The monopolistic-minded Anglo-Sicilian sulfur interests had kept brimstone prices high above what the market was willing to pay. The first World War created so strong a demand for more and higher-quality sulfuric acid that the swing started back to brimstone. By 1919 the total amount of acid derived from brimstone had increased to almost 50 per cent. Meanwhile, Herman Frasch developed his process for getting sulfur out of the salt domes of Louisiana. This development restored brimstone sulfur to its premier position as the source of world sulfur in the manufacture of sulfuric acid.

Today, in the United States alone, about 8.25 million tons of 100 per cent acid is made from brimstone, 1.25 million tons from pyrites, and about 0.75 million tons from other sources, mostly smelter gases. Two processes dominate the sulfuric acid industry: the chamber, and the contact (tables 1 and 2).

CHAMBER ACID

The earlier process and the one which kept its dominant position until the turn of the century, was the chamber. In this process, sulfur dioxide is led up from burners into acid through the packing of a tower where, meeting countercurrent a trickling stream of dilute sulfuric acid containing nitrous oxide, it is oxidized to sulfur trioxide. From this tower the trioxide goes into large lead-lined chambers (which give the process its name), where reacting with fine sprays of water, it forms hydrogen sulfate or sulfuric acid, which collects on the floor. The acid so formed is relatively weak—about 62 to 70 per cent strength, which corresponds to 50° to 55° Bé acid—and contains some impurities objectionable to the chemical industry.

CONTACT PROCESS

The chemical industry generally, however, had to have stronger and purer acid than the chamber quality, and its demand stimulated interest in contact processes. The first contact acid plants were relatively high in investment cost and rather difficult to operate. Their ability to compete at all with existing chamber plants was due primarily to their production of acid of higher strength and quality. Before the first World War only about 20 per cent of the country's sulfuric acid plants used the contact process; the number gradually increased, until in 1947 the production of contact acid comprised about 10 million tons out of a total of some 12 million tons. Most fertilizer companies still operate their old chamber plants; but replacements with contact plants is underway. The change-over is bound to continue. In the Baltimore area, for example, Mathieson and Davison, two of the largest producers, have each converted most of their acid production to the contact process.

In the contact process the conversion of sulfur dioxide to the trioxide is accomplished directly by means of a catalyst. Originally platinum was used as the catalyst; but impurities, such as arsenic, in the gases poisoned it, making it necessary to design a unit to reduce this hazard. The regeneration of the poisoned catalyst required elaborate purification equipment. The subsequent use of nonpoisonable vanadium catalyst overcame these shortcomings and undoubtedly was one of the factors favoring the installation of contact plants.

By the end of the first World War the contact process had not made much progress. The plants were designed almost entirely for handling pyrites, which involved extensive gas cooling and cleaning equipment between the roasters and the acid plant. Perhaps the only big improvement made at that time was to substitute sulfur and thus eliminate the dust factor. In that period a good chamber plant that could produce an acid of, say, 60° Bé had the advantage in acid cost over a contact plant; whereas for 66° Bé or stronger acid, the contact plant had the advantage.

Then in 1925 Monsanto introduced a perfected vanadium catalyst which was not affected by arsenic or chlorine, two elements that readily poisoned the platinum catalyst. This eliminated the elaborate purification facilities required with the platinum catalyst. Further improvements followed, and by the second World War acid manufacturers had available four-pass converter types of contact plants capable of converting more than 200 tons of acid a day. Today contact plants are designed, at much lower cost, capable of handling an 8 to 10 per cent sulfur dioxide with a 96.9 per cent conversion; a prewar plant rated at 150 to 160 tons a day is now capable of producing 200 tons with the addition of only a small amount of vanadium catalyst.

The contact process produces a much stronger acid than chamber acid and will not corrode iron, whereas chamber acid has to be kept in expensive lead-lined vessels. Less space is required in the contact process to produce the same amount of acid. Modern superphosphate manufacturers prefer using 56° Bé acid (71.2 per cent H_2SO_4). Higher strength contact acid can be diluted on the spot with the evolution of heat. Taking advantage of this heat, one can obtain the proper temperature of the acid for acidulation. Chamber acid, on the other hand, must be heated to the proper acidulating temperature, especially in northern regions during winter.

Financial considerations cannot be ignored, especially in the fertilizer industry, which operates on a narrow margin of profit. At today's prices, the capital investment, raw materials, and operating costs generally favor the contact process.

PYRITES AND BRIMSTONE

The relative position of pyrites and brimstone in the sulfuric acid industry has been suggested. Pyrites came into use when Sicilian sulfur was increased from $20 to $70 per metric ton. This sharp increase stimulated the search for satisfactory substitutes. In 1833 Michel Perret of France developed a process for getting sulfur dioxide from iron pyrites by roasting them at 900 to 1,000°F. Germany and other European countries quickly installed facilities. As improvements were made in the process, more units were installed, and by 1880 most European countries had completely switched to pyrites. The process did not make the same gains in the United States. Subsequently, discovery of sulfur in the salt domes of the Gulf States and the success of the Frasch process enabled brimstone to hold first rank in this country.

Brimstone has definite advantages over pyrites, primarily economic, which in the long run always determine the issue. Some comparisons will bring these out: First, only about 40 per cent of pyrites is converted to sulfur dioxide, as against 98 per cent of brimstone. Economies in freight, in fuel consumption, and in size of furnace grates favor sulfur burning. Pyrites produce an iron oxide residue which has to be handled, sintered, and nodulized to render it acceptable to the steel industry. These operations add to its shortcomings. The total cost of a pyrites roasting plant is roughly about 2.5 times that of a sulfur-burning plant. The labor and maintenance costs of the pyrites roaster plant make it relatively uneconomical If the chamber process is used with pyrites, the consumption of nitrous oxide is about twice as high as in a brimstone plant.

The use of pyrites at present, however, is by no means negligible. It is estimated that in 1948 about 5 million tons of pyrites were consumed, of which more than 1.25 million tons were obtained in Spain. Those interested in its survival are making improvements to maintain a competitive position. For example, one of the latest developments is flash roasting. This improvement involves a flotation process for concentrating ores, resulting in a product of 100- to 200-mesh size. These fines are fed into a vertical kiln from the top, and as they drop through a counter current of air they burn completely by the time they reach the floor of the kiln.

Pyrites and brimstone have been in competition many years. Which will eventually survive and dominate is anybody's guess. Economic factors will certainly give the ultimate answer. So long as brimstone can be obtained in as pure a form and at relatively low costs as at present in Texas and Louisiana, and so long as new salt domes are discovered, brimstone will perhaps dominate the American sulfuric acid scene. The competition between these two sources of sulfur is a healthy factor in our chemical industry.

SUPERPHOSPHATE

At present, 94 out of a total of 191 superphosphate plants, roughly half, have co-existing acid facilities. Some superphosphate manufacturers also obtain their acid requirements from the spent acid of the petroleum and explosives industries, and some get acid from ore smelters. As has been mentioned, the superphosphate industry operates on a narrow margin of profit, producing a low-cost commodity, and therefore must take advantage of every possible factor to keep the unit production cost down. The location of a plant close to a cheap, dependable source of acid is a distinct advantage. That, for example, is why so many superphosphate plants are located not far from the great Copper Hill plant of the Tennessee Corporation. The acid manufacturer starts production with sulfur dioxide. He burns brimstone or roasts pyrites to get the initial sulfur dioxide. Many ore smelters already have sulfur dioxide in sufficient strength in their gases to permit recovery and conversion to sulfuric acid. Some of these smelters produce superphosphate as a means of profitably utilizing such waste gases.

IMPORTANCE OF SULFUR FERTILIZERS TO PLANTS

Sulfur is recognized as an essential plant nutrient. Until recently, many agronomists took sulfur for granted. Recent investigations, however, have shown that in many soils here and abroad sulfur is deficient and has to be replenished to maintain crop yields. It is not fully appreciated in all quarters that the superphosphate industry has made a generous contribution to agriculture's sulfur requirements wherever its product has been used as a fertilizer. In the reaction between rock phosphate and sulfuric acid about half the weight of the resultant superphosphate is calcium sulfate. In other words, about 12 per cent of normal superphosphate is sulfur capable of feeding plants. The use of calcium sulfate or gypsum in agriculture as a source of calcium and sulfur is one of the oldest established practices. Benjamin Franklin was one of the first to sponsor it in our country. The superphosphate industry, strange to say, has in its sales efforts emphasized the phosphorus but ignored the sulfur portion of its product. Recognition should be given to this sulfur content. Farmers and agricultural workers should be made aware of its importance. Some persons clamor for higher analysis materials. To produce these it is often necessary to refine to a very high degree. For example, many insist on having a 48 per cent concentrated superphosphate in place of a 20 per cent grade. To produce the concentrated form by the wet process the manufacturer removes all the calcium sulfate portion, leaving virtually nothing but monocalcium phosphate. If concentrated were to supplant the 20 per cent grade, it would not be long before the soil in many parts of the country might become seriously low in sulfur, which would have to be applied separately as a nutrient. This sort of thing has occurred with potash salts: as kainit and other manure salts containing magnesia were replaced by refined, high grade muriate, it became necessary to apply magnesia to the depleted soils.

TABLE 3

*Sulfuric acid consumed by fertilizer industry in the United States (100 per cent basis), short tons and percentage of total**

YEAR	SHORT TONS	PERCENTAGE OF TOTAL CONSUMED
1939	1,225,000	24.6
1940	1,410,000	24.6
1941	1,556,000	22.7
1942	1,830,000	23.5
1943	2,500,000	28.8
1944	2,640,000	28.3
1945	2,850,000	31.1
1946	3,020,000	34.9
1947	3,510,000	35.2

* Source: Based on Chemical Engineering and Chemical and Metallurgical Engineering statistics.

Other fertilizer materials, of course, contain sulfur and help maintain sulfur supplies in soils. Among those used in large quantities are sulfate of ammonia with a sulfur trioxide content of about 60 per cent (59.67 per cent); sulfate of potash-magnesia, with about 57 per cent SO_3 (56.76 per cent); and 16–20 ammonium phosphate-sulfate, with about 39 per cent SO_3 (38.49 per cent). Superphosphate, by the way, has 29.09 per cent SO_3.

Evidently, then, sulfur occupies an important place in the fertilizer industry (table 3). It is closely linked with the manufacture of superphosphate, for which about 3.5 million tons 100 per cent basis sulfuric acid is used annually, and with such other fertilizer materials as sulfate of ammonia, 16–20 ammonium phosphate-sulfate, and sulfate of potash. Its importance as a plant nutrient should receive greater recognition by all who are concerned with agriculture.

SULFUR CONTENT OF VEGETATION

MOYER D. THOMAS, RUSSEL H. HENDRICKS, AND GEO. R. HILL[1]

American Smelting and Refining Company, Salt Lake City

Although sulfur is an essential constituent of vegetation, only limited information is available in the literature concerning the range of concentration of the element in normal and abnormal plants and the nature and distribution of the different sulfur compounds. As was pointed out by Hart and Peterson (4), the early analyses of vegetation, which were carried out on ashed material, are unreliable because most of the organic sulfur was lost in the ashing process. Values 2 to 100 fold higher have been found by the peroxide fusion methods or by one of the wet-ashing methods (3).

REVIEW OF LITERATURE

Peterson (9) in Wisconsin analyzed a number of different plants for sulfate, volatile, soluble, insoluble, and total sulfur. Cabbage and rutabagas contained 0.08 and 0.10 per cent volatile sulfur and 0.62 and 0.51 per cent total organic sulfur, respectively. Only trace amounts of volatile sulfur were found in alfalfa, sugar beets, clover, grains, and grass. Other organic sulfur values were as follows: alfalfa plants 0.18 and 0.28 per cent; clover 0.11 and 0.16 per cent; radish 0.17 to 0.40 per cent; dried rape 0.16 to 0.49 per cent; and sugar beet tops 0.38 per cent.

Shedd (10) analyzed soybeans, clover, and alfalfa plants from eight different counties in Kentucky and found total sulfur ranging from 0.20 to 0.30 per cent in soybeans; 0.21 to 0.30 per cent in clover, and 0.28 to 0.46 per cent in alfalfa. After subtraction of the sulfate sulfur, there remained as organic sulfur 0.15 to 0.26 per cent in soybeans; 0.13 to 0.16 per cent in clover; and 0.18 to 0.24 per cent in alfalfa. Sulfur fertilizer raised the total and sulfate values but did not change the organic fraction appreciably in clover and alfalfa. In the soybean there was a small significant increase in the organic sulfur.

Eaton (1) grew soybeans in sand culture with adequate and deficient supplies of sulfur. The plus-sulfur leaves carried 0.43 per cent total and 0.21 per cent organic sulfur. The minus-sulfur leaves carried 0.34 and 0.23 per cent respectively.

Miller (8) in Oregon made similar observations on clover and rape with and without addition of nitrate and various sulfates to the soil. The clover plants carried total sulfur ranging from 0.16 to 0.41 per cent, depending on the treatment. The organic sulfur ranged from 0.11 to 0.20 per cent and showed no consistent effect of sulfate fertilizers, though nitrate alone tended to lower the sulfur value below the check. Total sulfur in the rape plants ranged from 0.16 to 3.28 per cent, depending on fertilizer treatment; organic sulfur ranged from 0.11 to 0.43 per cent. Addition of sulfate to the soil increased the organic sulfur level of rape plants about 0.2 per cent.

Hall (2), who analyzed alfalfa plants from Illinois, Iowa, and Kansas, found contents of 0.37 to 0.56 per cent total sulfur and only 0.010 to 0.044 per cent sulfate sulfur. The differences, representing organic sulfur, are much higher than the organic sulfur values found by other investigators. The discrepancy appears to lie in the sulfate values.

Many investigators, for example, McCool and Johnson (6), and Katz and McCallum (5, p. 104), have shown that vegetation in urban and industrial districts absorbs sulfur dioxide from the atmosphere, causing a significant increment of the sulfur content of the leaves. The former found that on a given type of soil there was usually a decrease in the total and the sulfate sulfur of the plants with distance from the city center. This was true both for East St. Louis, Illinois, and for Camden, New Jersey. McCool and Mehlish (7) found that most of the soils in these two localities were not significantly affected by years of exposure to the industrial atmospheres. Titrable acidity of Yazoo clay and the sulfur content of Memphis silt loam decreased slightly but significantly with distance from the city centers of East St. Louis and St. Louis.

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[1] Grateful acknowledgment is made to F. S. Harris of the Utah State Agricultural College, George Stewart of the U. S. Forest Service, and A. F. Barney and L. V. Olson of our staff for collecting many of the samples of vegetation.

Katz and McCallum (5) were able to correlate the sulfur content of the leaves of trees and shrubs with distance down the narrow Columbia River Valley from the Trail Smelter. Douglar fir, which normally had about 0.10 per cent sulfur in its needles, accumulated sulfur until the 4- or 5-year-old needles had a range from 0.75 to 0.20 per cent, depending on the distance down the valley. Similar relations were found for yellow pine except that the sulfur range was from 0.60 to 0.15 per cent. Absorption of sulfur dioxide occurred during the growing season only and was practically zero during the winter months. Each year for 3 or 4 years the needles absorbed an appreciable increment of sulfur then remained unchanged in sulfur content for a year or two before being shed. Larch, hazel, ninebark, and aspen leaves absorbed about the same percentage of sulfur in one season as the nearby conifer needles absorbed in 4 years, and showed about the same sulfur gradient with distance down the valley as did the conifers.

Thomas, Hendricks, and Hill (13) fumigated alfalfa with sulfur dioxide and raised the total sulfur content of the leaves from 0.37–0.68 per cent to 0.81–2.26 per cent. The organic sulfur content of the leaves ranged from 0.23 to 0.29 per cent before fumigation and from 0.23 to 0.34 per cent after fumigation. Of the added sulfur 97 per cent was accounted for as sulfate. A significant increment of "labile" sulfur (probably cystine sulfur) amounting to 0.01–0.04 per cent was noted as a result of the fumigations. The increment was greatest when the nutrient solution was deficient in sulfur. A similar result was obtained with sugar beets. Other studies (11) in which the radiosulfur was supplied either as sulfur dioxide through the leaves or as sodium sulfate through the roots have shown that the sulfur is rapidly converted into organic form, which appeared to be largely cystine or methionine.

Thomas *et al.* (12) found 0.12 per cent sulfur in the tops or 0.26 per cent in the leaves of alfalfa growing in a nutrient solution deficient in sulfur. In a solution with adequate sulfur, the tops contained 0.30 and the leaves 0.60 per cent. The roots of these low- and high-sulfur plants had 0.05 and 0.20 per cent and the hair roots 0.37 and 0.83 per cent, respectively. The alfalfa showed sulfur-deficiency symptoms if the level in the nutrient solution fell below 2 p.p.m. sulfate sulfur.

MATERIALS AND METHODS

From 1935 to 1939 an extensive survey was made to determine the sulfur content of vegetation throughout the western part of the United States. Samples of many species of plants were collected in localities representative of as many ecological conditions as possible. Soils of low and high sulfur content were sought, including sulfur-deficient, normal, gypsum, and saline soils. Humid and arid regions were sampled. Urban and industrial environments were compared with isolated rural regions. Species having a wide distribution were collected to obtain as comprehensive a picture as possible.

Total sulfur analyses were made by the Parr bomb on 0.7-gm. samples of air-dried material. As none of the plants included in this study had an appreciable quantity of volatile sulfur compounds, air-drying was permissible. The bombed material was dissolved in hot water and acidified to a definite excess of 1 ml. of HCl. The solution was then filtered, diluted to about 350 ml. and precipitated hot with an excess of $BaCl_2$. After standing cold 1 day the solutions were stirred, and if necessary were "seeded" with a trace of $BaSO_4$. The solutions were then allowed to stand at least 5 or 6 days longer before filtration on No. 00 Swedish paper. The precipitates were ashed and weighed in platinum crucibles. With this technique, excellent concordance of duplicate determinations was invariably obtained, the maximum deviation between the duplicates being 1.5 mgm. $BaSO_4$, which is equivalent to 0.03 per cent sulfur in the vegetation. A large majority of the determinations agreed within 0.3 mgm.

The "seeding" operation and long standing seem to be necessary with materials containing less than 0.1 to 0.2 per cent sulfur. In some of the earlier analyses no precipitate was found in 3 days' standing, without "seeding." These samples frequently yielded 0.1 to 0.2 per cent sulfur when subsequently analyzed by the technique described. Even with larger amounts of sulfur there was a slight additional precipitation after 3 days' standing; it was considered advisable, therefore, to allow the solutions to stand about a week. A number of solutions allowed to stand several months gave no higher values than those obtained within a week.

Except for a few of the earlier analyses, in which there was insufficient material to repeat the determinations, all the results reported were obtained by the improved technique. Some of the determinations which yielded about 0.05 per cent of sulfur are believed to be somewhat low.

RESULTS

Table 1 summarizes total sulfur analyses of a large number of samples of leaves from trees, shrubs, and halophytic plants growing in rural regions throughout the 11 Western States, far removed from any industrial air pollution. The natural habitats of the plants were sampled primarily, but whenever possible, samples were also taken from saline or gypsum soils in the arid valleys, including a few halophytes from the "alkali" spots for comparison. Most of the leaf samples had rather low concentrations of sulfur, from 0.1 to 0.3 per cent. The conifer needles were particularly low, averaging 0.1 per cent, but a few samples were found with two to four times this amount. As already noted, Katz and McCallum (5) found 0.2 to 0.8 per cent sulfur in conifer needles from an industrial area. With the exception of single samples of locust, chokecherry, and elderberry, the only high concentrations were found in the populus, olive, and willow. These trees can tolerate, or even thrive in, a saline environment and their leaves can take up more than 1 per cent sulfur. The halophytes, except salt grass, had the expected large concentrations, which were mostly sulfate (plus chloride) (table 6). The salt grass seems to adjust itself to its environment by excluding the salt rather than by absorbing it. The others absorb large amounts of salt.

Table 2 gives total sulfur for the leaves, stems, and blossoms of alfalfa and sweet clover. Both rural and industrial areas are considered. The two legumes exhibit a 9 to 12 fold range of sulfur concentrations in their leaves. The range is much smaller in the stems and blossoms. The stems have about one fourth and blossoms about three fifths as much sulfur as the leaves. The leaves show wider variations in the rural than in industrial areas. This statement needs qualification. Plants in an industrial area should contain more sulfur than strictly comparable plants in a rural area because of absorption of sulfur dioxide, as is suggested by the higher minimum values of the former in table 2. Though the maximum values appear to be higher in the rural group, leaf sulfur as high as these maxima has been observed as a result of a long-time low-concentration fumigations with sulfur dioxide in the laboratory (13). The highest values for alfalfa (1.5–2.1 per cent) in rural areas were found on saline and gypsum soils low in chloride; the lowest values (0.18 per cent) were found in the Pacific

TABLE 1

Sulfur content of leaves of plants growing in nonindustrial areas throughout the 11 Western States

PLANTS	NUMBER OF SAMPLES	SULFUR (S) CONTENT		
		Minimum	Maximum	Average
		per cent	*per cent*	*per cent*
Conifers (pine, fir, spruce, and juniper)				
1st year needles	66	0.04	0.25	0.11
2nd year needles	73	0.07	0.37	0.11
3rd year needles	28	0.06	0.26	0.10
4th year needles	28	0.04	0.22	0.10
5th year needles	22	0.05	0.22	0.11
Deciduous trees				
Box elder	9	0.20	0.30	0.24
Locust	22	0.20	0.59	0.28
Maple	4	0.20	0.37	0.27
Oak	3	0.16	0.19	0.18
Peach, plum, and apple	8	0.11	0.28	0.20
Populus	39	0.20	1.16	0.48
Russian olive	14	0.32	0.80	0.50
Willow	52	0.13	1.11	0.54
Shrubs and bushes				
Chokecherry	13	0.04	0.87	0.19
Elderberry	14	0.11	0.83	0.28
Oak brush	6	0.12	0.24	0.17
Purshia	10	0.12	0.20	0.16
Sagebrush	22	0.14	0.37	0.24
Rabbit brush	11	0.20	0.45	0.31
Raspberry, serviceberry, snowberry, and squawberry	29	0.09	0.30	0.20
Halophytes				
Allenrolfea (bushy samphire)	2	1.18	1.78	1.48
Atriplex	14	0.41	1.70	0.88
Greasewood	13	0.35	1.15	0.58
Salicornia	3	0.70	3.48	2.04
Salt grass	5	0.28	0.48	0.34
Suaeda (ink weed)	3	1.70	3.51	2.94
Tamarix	13	1.76	2.89	2.36

Northwest on the sulfur-deficient soils derived from the extensive lava flows. The latter had little or no sulfate sulfur.

A number of alfalfa leaf samples from rural Utah are listed in table 3 along with the water-soluble sulfate and chloride in the soils on which they were growing. The leaf sulfur increased steadily with the soil sulfate when the chloride was low, but high chloride seemed to depress somewhat the absorption of sulfate.

TABLE 2

Sulfur content of leaves, stems, and blossoms of alfalfa and sweet clover growing in nonindustrial and industrial areas throughout the 11 Western States

NUMBER OF SAMPLES	RELATION TO INDUSTRIAL AREA	STEMS			LEAVES			BLOSSOMS*		
		Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average
					Alfalfa					
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
134	Out	0.07	0.35	0.14	0.18	2.11	0.62	0.19	0.47	0.34
86	In	0.08	0.39	0.17	0.50	1.16	0.74	0.30	0.51	0.40
					Sweet clover					
21	Out	0.05	0.42	0.21	0.20	1.80	0.67	0.32	1.25	0.46
3	In	0.23	0.26	0.21	1.01	1.13	1.07	—	—	0.63

* Number of samples: alfalfa, 23 in nonindustrial and 11 in industrial area; sweet clover, 12 in nonindustrial and 1 in industrial area.

TABLE 3

Sulfur content of alfalfa leaves growing on or near saline soils

LEAF SULFUR		WATER-SOLUBLE SALT IN SURFACE SOIL	
Normal	Chlorotic	Sulfate (S)	Chloride (Cl)
per cent	*per cent*	*ppm.*	*ppm.*
0.58	—	20	89
0.66	-	32	42
0.65	0.87	37	56
0.83	—	58	71
0.79	0.94	81	96
1.01	1.35	100	44
0.49	-	224	155
1.23		1100	340
1.09	—	1870*	17
1.46	—	3220*	40

* Gypsum.

Table 4 gives total sulfur in the leaves and stems of wheat, barley, oats, rye, and peas in nonindustrial and industrial areas. The comparatively low sulfur values in most of these samples reflect the low sulfur content of the soils on which they grew. Some of the oat samples, however, were taken from saline soils and contain more than 1 per cent sulfur. The contribution of industrial smoke is apparent in nearly all crops.

Table 5 summarizes total, sulfate, and organic sulfur and chlorine in the leaves of alfalfa plants growing in saline soils in nonindustrial areas of Utah.

TABLE 4

Sulfur content of leaves and stems of grain plants and peas growing in industrial and nonindustrial areas throughout the Western States

NUMBER OF SAMPLES	RELATION TO INDUSTRIAL AREA	STEMS			LEAVES		
		Minimum	Maximum	Aveage	Minimum	Maximum	Average
				Wheat			
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
20	Out	0.04	0.21	0.14	0.19	0.69	0.30
3	In	0.11	0.20	0.15	0.33	0.72	0.53
				Barley			
20	Out	0.07	0.27	0.16	0.17	0.61	0.41
5	In	0.13	0.27	0.20	0.52	1.00	0.82
				Oats			
9	Out	0.08	0.34	0.23	0.14	1.10	0.46
4	In	0.10	0.27	0.21	0.55	1.27	0.88
				Rye			
4	Out	0.09	0.15	0.12	0.14	0.41	0.29
1	In	—	—	0.14	—	—	0.74
				Peas			
8	Out	0.05	0.26	0.19	0.20	0.44	0.32
1	In	—	—	—	—	—	1.15
				Total for grains			
53	Out	0.04	0.34	0.16	0.14	1.10	0.39
13	In	0.10	0.27	0.19	0.33	1.27	0.70

Both green and chlorotic leaves are considered. The latter have more sulfur than the former, but the two groups of analyses overlap and it is probable that only those leaves with a very high sulfur content were chlorotic as a result of too much sulfate. The chlorine values of the two groups are similar and are roughly equal to the total sulfur values. The organic sulfur (total minus sulfate sulfur) has the same remarkably narrow range (about 0.2–0.4 per cent) which has been found for alfalfa in earlier work (11) and by other investigators (1, 8,

TABLE 5

Total, sulfate, and organic sulfur and chloride in alfalfa leaves in rural Utah

	TOTAL S	SO_4-S	ORGANIC S	Cl
Normal leaves				
	per cent	*per cent*	*per cent*	*per cent*
Minimum	0.38	0.20	0.18	0.45
Maximum	1.52	1.08	0.44	1.85
Average (14 samples)	0.86	0.54	0.32	0.91
Chlorotic leaves				
Minimum	0.48	0.26	0.22	0.52
Maximum	2.11	1.72	0.39	1.66
Average (6 samples)	1.17	0.90	0.27	0.95

TABLE 6

Sulfur fractions and chlorine in leaves of plants growing in saline soils in rural Utah

(Individual samples)

	TOTAL S	SO_4-S	ORGANIC S	Cl
	per cent	*per cent*	*per cent*	*per cent*
Grain	0.47	0.22	0.25	1.28
	0.55	0.30	0.25	0.73
Foxtail	0.44	0.17	0.27	1.77
Salt grass	0.48	0.21	0.27	1.11
	0.28	0.10	0.18	1.61
Poplar	0.87	0.44	0.43	0.22
	1.16	0.96	0.20	0.14
	0.43	0.27	0.16	0.41
Lambsquarter	0.79	0.51	0.28	2.78
	0.59	0.37	0.22	3.52
Poverty weed	1.70	1.39	0.31	1.62
	1.26	0.99	0.27	2.80
Atriplex	1.26	1.00	0.26	7.29
	0.65	0.48	0.17	7.24
	0.92	0.71	0.21	3.21
Greasewood	1.00	0.80	0.20	1.99
Inkweed (Suaeda)	3.51	3.33	0.18	8.77
	1.70	1.46	0.24	5.16
	2.60	2.29	0.31	4.54
Salicornia	3.48	3.20	0.28	4.82
	1.94	1.77	0.17	12.20
Tamarix	2.66	1.92	0.74	4.25
	2.89	2.18	0.71	2.94
	2.69	2.03	0.66	3.80
	2.17	1.54	0.63	3.25

9). This is true even though considerable amounts of chlorine were taken up at the same time.

Table 6 gives analyses similar to the alfalfa data in table 5 for 11 species of plants. The very large and variable uptake of sulfate and chloride, particularly by some of the halophytes, is striking, but the grains and grasses tend to exclude the sulfate while taking up appreciably more chloride. Again the range of organic sulfur values is restricted and corresponds to the range in alfalfa for all the plants in table 6 except tamarix. The latter has appreciably higher organic sulfur (about 0.7 per cent) and is comparable with rutabagas and cabbage (9).

In table 7 total sulfur values are given for the leaves of plants growing near hot sulfur springs at Steamboat Springs, Colorado, and Thermopolis, Wyoming. The lodge pole pine needles came from geyser areas in Yellowstone Park. The latter carried up to three times their normal amount of sulfur (0.12 to 0.30 per cent). They also showed some die-back at the tips, the cause of which is not known. It is possible that the needles acquired their excess sulfur from the air because the sulfate content of the soil was low and there is usually a faint odor of hydrogen sulfide near the pools and geysers. At considerable distances from the geysers, the sulfur content of the needles was normal. It must be noted that the needles of various ages on a tree up to 5 or 6 years had about the same sulfur content and did not usually show a trend toward increasing concentration with age. There is even a tendency for the first-year needles to contain a little more sulfur than the older needles. This would not be expected if the absorbed gas were sulfur dioxide (5).

TABLE 7

Sulfur content of leaves of plants growing near hot sulfur springs in Colorado and Wyoming and near geysers in Yellowstone Park

	NUMBER OF SAMPLES	SULFUR CONTENT		
		Minimum	Maximum	Average
		per cent	*per cent*	*per cent*
Lodge pole pine needles	21	0.12	0.29	0.19
Alfalfa	3	0.87	1.51*	1.14
Broad-leaf grass	3	1.01†	2.62†	1.55†
Sunflower	2	1.05†	1.68†	1.36†
Poplar	2	0.83	1.78	1.30
Russian olive	1	—	—	1.24
Willow	8	0.31	1.10	0.47
	—	—	1.70‡	—

* Vigorous, healthy plant of good color.

† Acute plus chlorotic markings.

‡ Chlorotic leaves on willow.

At Steamboat Springs and Thermopolis the vegetation was greatly enriched in sulfur, mostly because of gaseous absorption probably as hydrogen sulfide at the former but partly because of high soil sulfate at the latter. The broad-leaf grass and the sunflowers hung partly over the big hot pool at Thermopolis and showed typical gas injury, both acute and chlorotic. Here the odor of hydrogen sulfide was distinct, but sulfur dioxide was not identified by odor. The old leaves of the grass carried 2.62 per cent sulfur, the young leaves 1.01 per cent. Similarly, the old and young leaves of the sunflower had 1.68 and 1.05 per cent. These high concentrations together with the typical gas lesions suggest that the sulfur was absorbed principally in gaseous form.

SUMMARY

Nearly one thousand samples of vegetation collected throughout the 11 Western States have been analyzed for total sulfur in the leaves. Sulfate and chloride have been determined on many of these leaf samples and also on representative stems and blossoms from the same plants and on the soils on which the plants grew. Total leaf sulfur can vary over a wide range depending on the supply from the soil or the atmosphere. A twelvefold range in total sulfur has been noted for alfalfa leaves with sulfur supply from either soil or atmosphere. Some species may have a still greater range. The sulfate range parallels the total sulfur range. It is assumed that total sulfur minus sulfate represents organic sulfur. The latter exhibits a remarkably narrow range in the leaves of many species, usually falling between about 0.2 and 0.4 per cent on the dry-weight basis. The lower range indicates sulfur deficiency, and the upper range is not appreciably exceeded regardless of how much excess sulfate is present. The needles of conifers normally have smaller amounts, about 0.1 per cent, whereas tamarix and the crucifers and some other species with volatile sulfur compounds—onion, rape, radish—may have 0.5 to more than 0.7 per cent organic sulfur.

The halophytes generally adjust themselves to their environment by absorbing large amounts of chloride and sulfate. Salt grass effectively excludes salt.

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SULFUR METABOLISM IN ALFALFA

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In the preceding paper, sulfate, organic, and total sulfur values of many species of plants were considered with special reference to the sulfur supply from the soil and the atmosphere. In this paper attention is directed in more detail to the uptake and translocation of sulfur in alfalfa and the effect of sulfur on nitrogen metabolism. Only the vegetative processes of the plant are considered. No work has been done as yet on the flowers or seeds of alfalfa.

The essentiality of sulfur in the plant is doubtless due in large measure to the fact that sulfur amino acids are essential constituents of plant proteins. A close connection between sulfur and nitrogen metabolism must therefore exist. Sulfur deficiency is manifested by a yellowing of the leaves, suggesting that sulfur is indirectly involved in chlorophyll metabolism. Perhaps it is also involved directly through the protoplasm of the chloroplasts. Eaton (1, 2, 3) and Nightingale *et al.* (4) found that sulfur-deficient soybeans, sunflowers, mustard, and tomatoes have more nitrate, more soluble nitrogenous compounds such as amides and amino acids, and more of at least some forms of carbohydrates than do plants with adequate sulfur. This was considered to be due, first, to a lowered rate of nitrate reduction; second, to inability to synthesize proteins because of presence of insufficient sulfur amino acids; and third, to considerable proteolysis in the stems.

MATERIALS AND METHODS

Alfalfa was grown in large sand culture beds (5) in 1939, and again in 1940 and 1941. High and low levels of the principal nutrients and also different levels of sulfate from deficiency to adequacy were maintained in these beds. Half the plots were fumigated with sublethal concentrations of sulfur dioxide. Some phases of these experiments have already been published, including details of the apparatus, experimental procedure, yield, sulfur fractionation, and sulfur balance (6, 7, 8). In 1948 a number of absorption and translocation experiments on alfalfa were carried out with radiosulfur[1] (8), which was added either as sodium sulfate to the nutrient solution or as sulfur dioxide to the air. The radiosulfur therefore entered the plants through the roots or the leaves. In one translocation experiment, the ends of a few stems on several plants were dipped in a strong solution of radiosulfate.

RESULTS

Sulfur and nitrogen metabolism

The sulfur-deficient plants were chlorotic as described by Eaton and by Nightingale. Analysis of the 1939 to 1941 crops (6) showed that the chlorophyll in some sulfur-deficient leaves was as low as 60 per cent of the concentration in the normal plus-sulfur leaves. The sulfur dioxide fumigations prevented loss of chlorophyll. Similar relations, not reported earlier, were found for carotene and xanthophyll.

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[1] Supplied by Atomic Energy Commission, Oak Ridge, Tennessee.

TABLE 1

Balance sheet of nitrogen lost from nutrient solutions and found in 1940 and 1941 alfalfa crops and roots

	HIGH SULFUR			MEDIUM SULFUR			MEDIUM LOW SULFUR			LOW SULFUR		
	A* *gm.*	B* *gm.*	Gain $\frac{B-A}{B}$ *per cent*	A *gm.*	B *gm.*	Gain $\frac{B-A}{B}$ *per cent*	A *gm.*	B *gm.*	Gain $\frac{B-A}{B}$ *per cent*	A *gm.*	B *gm.*	Gain $\frac{B-A}{B}$ *per cent*
High nitrogen level—check plots												
1940 crops.......	240	135		210	121		224	91		171	64	
1941 crops.......	429	344		511	335		425	306		389	286	
1941 roots.......		72			80			86			99	
Total..........	669	551	−21	721	536	−34	649	483	−34	560	449	−25
High nitrogen level—fumigated plots												
1940 crops.......	237	125		219	122		208	108		179	91	
1941 crops.......	393	317		408	328		428	314		330	274	
1941 roots.......		79			73			73			79	
Total..........	630	521	−21	627	523	−20	636	495	−29	509	444	−15
Low nitrogen level—check plots												
1940 crops.......	185	115		199	126		170	87		168	74	
1941 crops.......	133	198		142	197		148	152		139	148	
1941 roots.......		56			58			49			54	
Total..........	318	369	+14	341	381	+11	318	288	−10	307	276	−11
Low nitrogen level—fumigated plots												
1940 crops.......	184	116		163	106		178	124		182	111	
1941 crops.......	120	167		142	185		145	166		139	156	
1941 roots.......		46			49			46			44	
Total..........	304	329	+8	305	340	+10	323	336	+4	321	311	−3

* A = nitrogen lost from nutrient solutions; B = nitrogen found in vegetation.

Nitrogen determinations were made on the leaves, stems, and roots of the 1940 and 1941 crops. The nutrient solutions were analyzed for nitrate and ammonia. From these data, the amount of nitrogen which disappeared from the nutrient solutions could be compared with that found in the vegetation. The results are summarized in table 1. With a high-level nitrogen supply (about

100 ppm.) in the nutrient solution, 15 to 34 per cent more nitrogen disappeared from the solutions than was found in the crops. The sulfur level in the nutrient solution had no significant effect on the nitrogen loss. No information is available as to the chemistry of this loss, but presumably elemental nitrogen was formed. There were few, if any, nodules on the roots of these plants, whereas the low-level nitrogen plants had many nodules. The high-nitrogen plots contained much more total nitrogen than the low-nitrogen plots, as indicated in table 1, but this was due largely to the fact that the former plants were larger, though the nitrogen content was also a little higher in general (table 2).

TABLE 2

Nitrogen content of leaves and stems of 1940 and 1941 alfalfa grown in nutrient solutions of high and low nitrogen level and also at four levels of sulfate

	HIGH SULFUR			MEDIUM SULFUR			MEDIUM LOW SULFUR			LOW SULFUR		
	Leaves *per cent*	Stem *per cent*	Roots *per cent*	Leaves *per cent*	Stems *per cent*	Roots *per cent*	Leaves *per cent*	Stems *per cent*	Roots *per cent*	Leaves *per cent*	Stems *per cent*	Roots *per cent*
High nitrogen level—check plots												
1940	4.8	1.9	—	4.9	2.1	—	5.1	2.4	—	5.4	2.9	—
1941	5.0	2.3	2.1	5.0	2.2	2.1	4.9	2.3	2.3	5.8	3.4	3.5
High nitrogen level—fumigated plots												
1940	4.9	2.0	—	4.9	2.1	—	4.9	2.1	—	4.9	2.2	—
1941	5.0	2.4	2.1	5.1	2.2	2.0	5.0	2.3	2.2	4.9	2.6	2.6
Low nitrogen level—check plots												
1940	4.9	1.9	—	4.9	2.0	—	4.6	2.0	—	4.7	2.6	—
1941	4.4	1.7	1.2	4.4	1.7	1.2	4.2	1.6	1.0	4.1	1.3	1.1
Low nitrogen level—fumigated plots												
1940	4.9	2.0	—	1.9	2.1	—	4.7	2.1	—	4.9	2.1	—
1941	4.2	1.7	1.1	4.4	1.7	1.2	4.3	1.7	1.0	4.1	1.6	1.0

In the plots with a low nitrogen level, and the higher sulfur levels, more nitrogen was found in the vegetation than was taken from the nutrient solution. The roots of these plants were well supplied with nodules, which evidently fixed elemental nitrogen more rapidly than nitrogen compounds were decomposed. With both low nitrogen and inadequate sulfur, however, net nitrogen losses were about 12 per cent. These losses were virtually eliminated by the fumigation treatments. It may be noted that in the low-nitrogen plots the actual nitrogen losses from the nutrient solutions were virtually independent of the sulfur level. In the low-sulfur unfumigated plots the uptake of nitrogen was less, primarily because the plants were smaller, since the nitrogen content of these plants was not materially different from that of the high-sulfur plants (table 2).

The total nitrogen of the leaves, stems, and roots of these plots are given in table 2. In the high-nitrogen check plots, the nitrogen content of the leaves, stems, and roots of the most sulfur-deficient plants was 15, 50, and 65 per cent higher respectively than that of the high-sulfur plants. The fumigated plots had no excess nitrogen in the leaves and only a slight excess in the stems and roots. Fractionation of the nitrogen was carried out on a few of these high- and low-sulfur leaves. The analyses indicated higher soluble amide and amino values in the low-sulfur leaves, but the nitrate values were inconclusive.

In the low-nitrogen group of plots the leaves that were most deficient in sulfur had a slightly lower nitrogen content than those with more sulfur. The sulfur-deficient stems were 25 per cent higher in nitrogen in 1940 and 20 per cent lower in 1941 than those with more sulfur. The fumigated plants had a uniform nitrogen content independent of the sulfur content. The enrichment of the leaves in nitrogen which characterized the high-nitrogen–low-sulfur plants was thus absent in the low-nitrogen–low-sulfur plants. If the explanation of Eaton is accepted for the enrichment, it seems likely that with low nitrogen supply the amount of nitrate reduced would fall off and the synthesis of protein could keep pace in spite of inadequate sulfur supply.

Sugar determinations have been made on the leaves of the alfalfa. Because the plants were harvested in the early hours of the morning when carbohydrates would be largely translocated out of the leaves, the sugar values were generally less than 2 per cent, and differences between plots were too small to be highly significant. In general, there was more reducing sugar and sucrose in the sulfur-deficient leaves and in those with low nitrogen than in the high-sulfur–high-nitrogen leaves, supporting the observations of Eaton and of Nightingale, who found that carbohydrates tend to accumulate in minus-sulfur plants.

Uptake by alfalfa of radiosulfur as sulfate from the nutrient solution is shown in figure 1. With a single dose of radiosulfate at 0 time, the maximum leaf concentration was attained in 2 weeks by plants that were slightly sulfur-deficient. The different organic sulfur fractions (6, 7) and also sulfate were present in approximately equal amounts for about 3 weeks; then the sulfate fell off to a very low value. The root sulfur reached its maximum value in a few days then remained constant. Evidently the radiosulfate was taken up into the leaves rapidly at first; then as the supply in the solution became exhausted, continued growth of the plant caused a reduction in the leaf concentration due to distribution through an expanding mass of tissue. The conversion of sulfate into organic forms appears to be less rapid in alfalfa than in tomatoes or sugar beets because this conversion was complete in the latter species almost as soon as it was absorbed, but with alfalfa the sulfate level remained appreciable until the supply was exhausted. Then it fell to a very low level.

Figure 2 shows a different type of experiment. At 0 time, radiosulfate was added to the nutrient solution of a low-sulfate plot, some plants of which had been harvested that day. Stems and roots of the unharvested plants were sampled at intervals during the first week after this treatment. These showed a slow uptake of sulfur, which was largely converted into organic sulfur

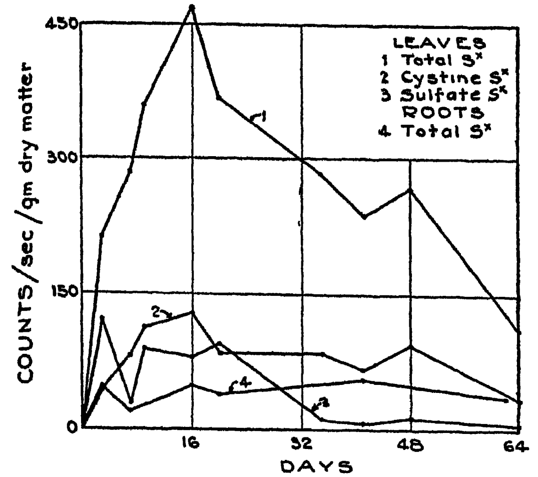

FIG. 1. ABSORPTION OF RADIOSULFUR IN OLD-GROWTH LEAVES AND IN ROOTS OF SULFUR-DEFICIENT ALFALFA PLANTS AND TRANSFORMATION OF SULFATE INTO ORGANIC SULFUR COMPOUNDS.

Curves for soluble and insoluble organic fractions similar to the cystine fraction are omitted.

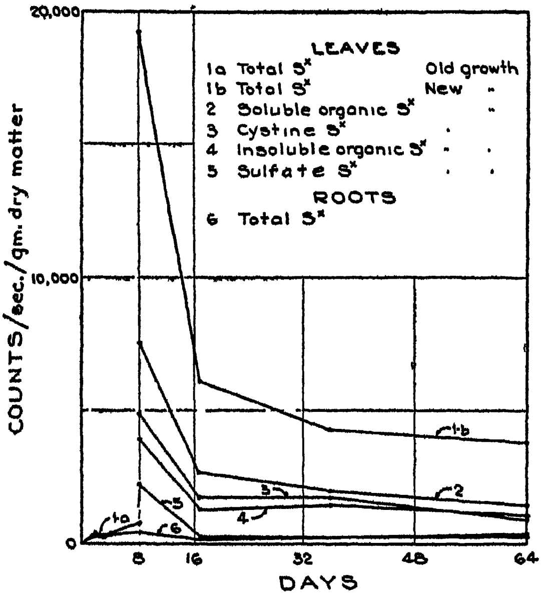

FIG. 2. ABSORPTION AND TRANSFORMATION OF RADIOSULFATE IN OLD- AND NEW-GROWTH LEAVES AND IN ROOTS OF ALFALFA

The new-growth, 8-day leaves were formed after the radiosulfate was added to the nutrient solution at 0 time.

compounds in both leaves and roots. The new leaves that grew on the harvested plants were sampled after 8 days' growth and were very rich in radiosulfur.

They contained 25 times the concentration of the old leaves. Thereafter, the plants grew rapidly, and radiosulfur concentration fell off sharply. Sulfate was a minor part of the mixture after the first sampling. The three organic sulfur fractions were not greatly different in amount. The roots picked up a small amount of radiosulfur during the first few days, and thereafter the root sulfur was constant. On the eighth day, root concentration of radiosulfur was 50 per cent of the old leaves but only 2 per cent of the new leaves. Obviously, radiosulfur was extensively used to supply the sulfur demands of the new leaves, but it did not add appreciably to, or displace, the sulfur already present in the old leaves.

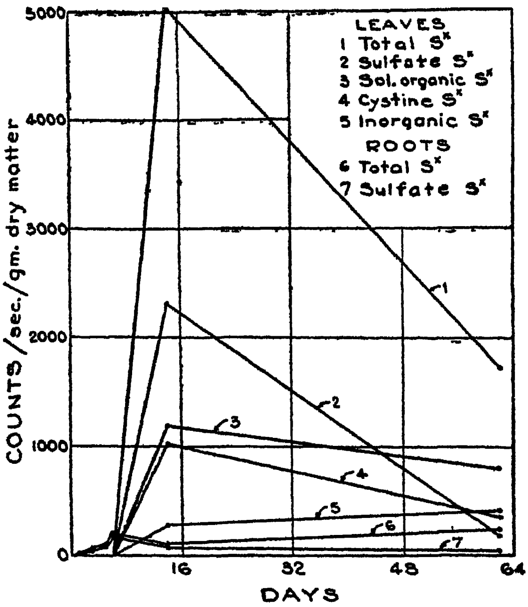

FIG. 3. ABSORPTION AND TRANSFORMATION OF RADIOSULFATE IN NEW-GROWTH LEAVES AND IN ROOTS OF ALFALFA

No new growth was allowed to start until 6 days after the radiosulfate was added to the harvested plot.

Figure 3 shows a similar experiment in which the plants were all harvested 2 days before addition of radiosulfate to the nutrient solution. For 6 days following this addition, no top growth of the plants was allowed. Only 40 per cent as much radiosulfur was used in this as in the preceding experiment. Samples of the roots showed that in 6 days only a small amount of the radiosulfate was absorbed—relatively about the same amount as in the previous experiment, with top growth present. In the roots without tops the absorbed sulfur was nearly all sulfate at the end of the first week, whereas in the roots with tops the sulfate had been changed during the first week almost entirely to organic form. For the following 2 months the level of sulfur in the roots remained essentially unchanged, as before, but the sulfate disappeared almost entirely. The leaves on the new shoots were very rich in radiosulfur, as in the previous experiment, the uptake being only little less than before.

Figure 4 describes a translocation experiment. The ends of several 4-foot stems of alfalfa on each of three plants were bent over and immersed in a beaker containing a strong solution of radiosulfate. A high concentration was absorbed locally and translocated continuously to other parts of the plant. After 1, 2, or 5 days' exposure, the immersed portion of a plant was carefully cut off and discarded; then the remainder of the plant was uprooted. Samples of leaves on the dipped and undipped stems were kept separate, and the roots were also sampled. The data for the three plants are shown in the graph. The upper curve indicates that after an initial rapid absorption, the total radiosulfur in the leaves on the stems that were dipped was nearly proportional to the time of dipping. Of this sulfur, 75 per cent was sulfate after 1 day but only 30 per cent was sulfate after 5 days. An appreciable amount of sulfur was carried down into the roots, then up into the stems that were not dipped. The leaves on the latter stems received about 10 per cent as much sulfur as the leaves on the dipped stems. All leaves had a higher concentration than the roots. Clearly a large amount of radiosulfur passed through the roots or at least through the root crowns, presumably as sulfate. That which remained in the roots was largely organic.

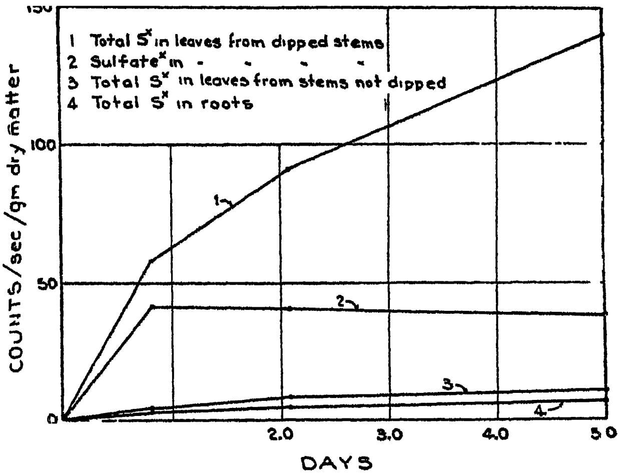

FIG. 4. TRANSLOCATION AND TRANSFORMATION OF RADIOSULFATE IN ALFALFA AFTER ABSORPTION FOLLOWING DIPPING OF THE ENDS OF A FEW STEMS OF THREE PLANTS FOR VARIOUS TIMES IN A STRONG SOLUTION OF RADIOSULFATE.

In a sulfur dioxide experiment, the expected result was obtained, namely, a high initial concentration in the leaves followed by some distribution throughout the plant. The roots never attained more than a few per cent of the leaf concentration, as might have been expected from the chemical data presented earlier.

SUMMARY

Alfalfa was grown in nutrient solutions containing high and low nitrogen levels and also high and low sulfate levels.

A balance sheet was prepared comparing nitrogen losses from the solutions with nitrogen found in the plants. A large amount of nitrogen was unaccounted for in the plants growing in the high-nitrogen solution. With low nitrogen and inadequate sulfur there was small loss of nitrogen, but with low nitrogen and adequate sulfur more nitrogen was found in the plants than was lost from the solution. Nodulation was marked on the roots of the low nitrogen plants, but the high-nitrogen plants were nearly free of nodules.

High-nitrogen–low-sulfur plants had an appreciably higher nitrogen concentration than all other plants. This excess nitrogen was soluble amide, amino, and possibly nitrate nitrogen.

In tracer experiments with alfalfa the concentration of radiosulfate in sulfur-deficient leaves reached a maximum in 16 days, then fell off as the plants grew. The sulfate was converted gradually but after 34 days almost completely into organic form. When harvested plants were treated with radiosulfur, the new growth took up much larger amounts of radiosulfur, and transformation to organic form was rapid. No sulfate in the roots was changed into organic form unless top growth was present. A translocation experiment showed that the radiosulfate could be absorbed through the ends of the stems dipped in a solution of radiosulfate. The absorbed sulfate was translocated down the stem and changed steadily into organic form. Some passed down through the crowns or roots and appeared in the leaves of undipped stems on the same plant, where it was also changed to organic form.

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SULFUR STUDIES OF INDIANA SOILS AND CROPS

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Improved crops capable of higher yields and improved soil management practices are making ever-greater demands upon the fertility of our soils. Increased use of higher analysis fertilizers has resulted in a smaller return to the soil of sulfur and other elements commonly included in lower analysis materials. The higher analysis fertilizers do not usually contain the sulfur of $(NH_4)_2SO_4$ or the sulfur of gypsum. Ordinary 20 per cent superphosphate contains 50 per cent gypsum. Sulfur, which is contained in plants in quantities similar to those of phosphorus, may become a limiting factor in crop production on many of our soils. Large areas deficient in sulfur for maximum plant growth have already been reported in Minnesota, Washington, and Oregon (1, 3, 11, 21, 22, 30). Other states—Alabama (31), Arkansas (32), California (15), Florida (5, 14), Idaho (20), Iowa (6, 10), Ohio (4), and Montana (7)—have reported responses to sulfur. Crocker (8) recently summarized the general subject of sulfur deficiency in soils.

Although sulfur shares many properties in common with phosphorus as a plant nutrient, it has other properties which complicate the problem of evaluating the level of sulfur fertility in the soil. It forms soluble compounds subject to leaching. The atmosphere contains variable amounts of sulfur compounds in gaseous form, and these are returned to the soil through precipitation and through direct absorption by the soil (2).

The purpose of this paper is to report the progress of sulfur studies conducted for 3 years, beginning in 1946, on the soils and crops of Indiana. This study had three main objectives: (*a*) to determine the sulfur balance in Indiana, (*b*) to determine the effect of sulfur as a soil amendment on certain Indiana soils, and (*c*) to determine the effect of sulfur upon the nutrient value of certain Indiana crops.

BALANCE SHEET OF SULFUR IN INDIANA SOILS

In striking a balance of the sulfur status of the soils of any region, the following factors must be appraised:

Sulfur brought down in the precipitation.
Sulfur removed by the various crops.
Total sulfur reserves present in the soil and their rate of release for crop use.
Sulfur directly absorbed by the soil from the atmosphere.

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[1] Journal Paper No. 430, Purdue University Experiment Station, Lafayette, Indiana; contribution from the department of agronomy. The authors are now at State College of Washington; U. S. Department of Agriculture, Beltsville, Md.; and North Carolina Agricultural Experiment Station, respectively. Acknowledgments are made to N. J. Volk, who proposed the research; to M. L. Jackson, who directed the initial phases; and to the Texas Gulf Sulphur Co., for fellowship funds that helped make this study possible.

Sulfur directly absorbed by the crop from the atmosphere and used in nutrition.
Sulfur annually leached from the soil.
Sulfur lost by erosion.
Sulfur returned to the soil in crop residues, manures, and commercial fertilizers.

Sulfur brought down in precipitation

Studies were begun in September 1946 to determine the amount of sulfur brought down in the precipitation. Twelve all-weather rain gauges were designed and constructed (12) and were placed at twelve locations over the state. Farmers cooperated by collecting the samples of precipitation and shipping them in for analysis. Sulfur was determined by a modification of the method introduced by Schroeder (23) in 1933. In this method, the sulfur is determined as the sulfate by titration, tetrahydroxyquinone being used as an internal indicator.

TABLE 1

Sulfur in precipitation at 11 locations in Indiana in one year, September 1, 1946 to August 31, 1947

LOCATION	TOTAL SULFUR	TOTAL* RAINFALL
	lb./A.	*in.*
Nashville	20.0	39.1
Gary	127.1	31.9
Monterey	27.4	34.2
Orland	25.8	37.1
Indianapolis	32.6	36.6
Rising Sun	29.7	40.7
Evansville	29.0	40.6
Montgomery	27.7	42.1
Larwill	23.2	35.6
Branchville	30.4	41.5
Lafayette	21.7	37.9

* Rainfall data are from official rain gauges in close proximity to these gauges from September 1, 1946 to August 31, 1947.

Table 1 summarizes the data on sulfur additions through the precipitation for Indiana during the year beginning September 1, 1946. The analyses were made on samples from the all-weather rain gauges and the amount of rainfall was taken from the nearest official rain gauge. The amount of sulfur brought down in the precipitation is relatively high in Indiana, ranging from 20 to 127 pounds per acre per year. Alway *et al.* (2) reported that the annual fall of sulfur in rain, snow, and dust in Minnesota ranged from less than 5 pounds per acre in the northern part of the state to more than 100 pounds in the industrial area around Minneapolis. The upper limits of sulfur additions are similar in the two states, but the chief difference is in the minimum additions. It appears that the likelihood of a sulfur deficiency under normal cropping conditions is less in Indiana than in Minnesota. The lowest value in Indiana is more than twice as high as the critical limit for sulfur deficiency, which was determined by Alway

(1) to be about 10 pounds per acre per year under Minnesota cropping conditions.

It is difficult, however, to set a hard and fast line between sufficiency and deficiency based upon sulfur brought down in the rainfall, since local factors may complicate the picture. Among these are kind of crop, length of growing season, level of fertility, extent of leaching, and sulfur reserves in the soil.

Sulfur removed by the chief crops

The sulfur and phosphorus requirements of many of our important agricultural crops are similar. The sulfur demands of some of these crops of importance in Indiana agriculture range from 8 to more than 30 pounds per acre per year (16). These estimates are shown in table 2.

Total sulfur reserves in soils

The sulfur soluble in 6 *N* HCl in the soils of Indiana was determined for the soil survey.[2] The total sulfur by this method ranged from 160 to 1,120 pounds per acre 6 inches; most of the soils contained 300 to 600 pounds. Since the sulfur of acid soils is contained in the organic matter, it would seem no more desirable to exploit this completely than to use all the nitrogen and phosphorus in soils for crop production. The reserves of all these may already be at a rather critical level, therefore, they should perhaps be regarded as a revolving fund rather than a checking account for eventual liquidation. Studies are in progress to determine the difference in total sulfur levels between our virgin and cropped soils to ascertain how rapid has been the depletion of our sulfur reserves.

TABLE 2

*Removal of sulfur and phosphorus by crops common to Indiana agriculture**

	YIELD PER ACRE	POUNDS REMOVED PER ACRE	
		Sulfur	Phosphorus
Corn ..	100 bushels	16.0	23.0
Wheat.	50 bushels	10.2	16.0
Potatoes	400 bushels	32.6	17.0
Alfalfa ..	4 tons	23.0	18.0
Tobacco..	5000 pounds	8.4	7.0

* Based upon data by Lipman and Conybeare (16).

Sulfur absorbed directly by the soil

No work was done to determine the amount of sulfur absorbed directly by the soil in Indiana. Alway *et al.* (2) evaluated this quantity of sulfur under Minnesota conditions, which might be expected to be somewhat similar to those in Indiana. They used a lead peroxide method to estimate the amount absorbed directly by the soil. Then they exposed to the atmosphere, but protected from rain, 100 sq. cm.

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[2] These determinations were made by Roy Weaver and George Enfield.

of cotton fabric and determined the amount of sulfur absorbed. By comparison with the amount absorbed in soils under controlled conditions, a correction factor was determined. The amount absorbed directly by the soil was comparable to the amount brought down in the rainfall.

Sulfur absorbed directly by the crop and used in nutrition

Although the SO_2 concentration of the atmosphere is only approximately 0.05 ppm., whereas the carbon dioxide content is approximately 315 ppm., direct absorption of SO_2 by plants is possible. In fact, several workers have investigated this potential source of sulfur (24, 25, 26, 27). Their experiments indicated that plants are able to utilize atmospheric SO_2. In none of the experiments where SO_2 was supplied to the tops, however, were the roots and the growth medium sealed off from the SO_2-containing atmosphere in contact with the aerial parts of the plants. This did not preclude the absorption of the SO_2 via the roots in the soil solution. By the use of S^{35} Fried (13) proved conclusively that alfalfa plants can absorb SO_2 directly through the leaves. Alfalfa plants were grown in a large glass chamber with their roots effectively sealed off from the atmosphere of the aerial portion of the plants. The aerial portion was exposed to SO_2 containing S^{35}. After 48 hours, the S^{35} was detected in the nutrient solution of the roots, indicating that the SO_2 had entered the leaves and permeated the entire plant. The S^{35}-SO_2 was removed from the atmosphere of the aerial portion of the plants, and the nutrient solution was changed then and at daily intervals thereafter. Ten days later the plants were harvested. The different sulfur fractions of the plants were tested for radioactivity. The results, summarized in table 3, show that the SO_2 was metabolized in the plant. Both soluble and insoluble organic fractions showed high counts as compared to the count found in the inorganic fraction.

TABLE 3

Radioactivity found in different sulfur fractions of alfalfa plants exposed to radioactive SO_2 and then allowed to elaborate the sulfur for 10 days

FRACTION	COUNTS PER MINUTE*			
	Tank 2	Tank 4	Tank 6	Tank 8
Inorganic	341	290	467	301
Soluble organic	4033	3083	4098	4703
Insoluble organic	4655	4000	4700	5123

* The greatest counting error involved was less than 1 per cent.

The rapidity with which the radioactive sulfur permeated the entire plant and the fact that the S^{35} was elaborated into the organic constitutents demonstrated conclusively that the SO_2 of the atmosphere is taken into the plant in a manner similar to the absorption of CO_2. Alway *et al.* (2) estimated the amount of SO_2 absorbed directly by the plant from the atmosphere and concluded that though this was a constant source of sulfur it could be expected to be absorbed only in the weight ratio of sulfur to carbon in the atmosphere, which is about 1:2400.

Since the weight ratio in the alfalfa plant is about 1:150, this was not a major contribution to the sulfur supply. Calculations based on this assumption suggest that not more than 6 per cent of the crop's requirements would be met by this source of sulfur, and perhaps the amount may be considerably less. Further study is needed to appraise the amount of the crop's requirements satisfied directly through the atmospheric source of SO_2.

Sulfur leached and lost by erosion annually from the soil

A number of investigators (9, 16, 17, 18) have measured the loss of sulfur from soils due to leaching. Although a number of factors determine this loss, those which prevailed where data were collected by Lyon and Bizzell (17) at Ithaca, New York, would seem comparable to those in most parts of Indiana. Using lysimeters 4 feet deep, these investigators found that approximately 37 pounds of sulfur per acre per year was lost by leaching. Lipman and Conybeare (16) estimated that about 6.1 pounds of sulfur per acre is lost annually in the process of erosion, which carries away the organic matter containing the reserve sulfur supply of the soil.

Return of sulfur in crop residues, manure, and fertilizers

Lipman and Conybeare estimated in 1930 that the average return of sulfur in crop residues, manure, and fertilizers was 3.9, 0.5, and 0.9 pounds per acre respectively, giving a total of 5.3 pounds. Much larger amounts of fertilizer are now applied in Indiana than were used in 1930. The higher analysis fertilizers coming into use contain less sulfur, higher yields removing more sulfur are now obtained, and with the switch to tractors possibly less manure and residues go back to the land. All of these factors would tend to counterbalance the increase in sulfur return to the soil through use of a greater tonnage of fertilizer.

It is estimated that about 45,000 tons of sulfur was applied in the superphosphate of fertilizers used in Indiana in 1948.[3] On the basis of uniform distribution over the 11 million acres of crop land, the annual return of sulfur through fertilizers would be approximately 8 pounds per acre.

Summary of gains and losses of sulfur in soil

Table 4 summarizes the estimates of gains and losses of sulfur in soils of Indiana. The difference between gains and losses of sulfur leaves a slight margin of gain beyond the requirements of most field crops as set down in table 2. These estimated averages do not give the true picture, since they tend to balance out the deficient areas with the surplus areas. The possibility remains that local areas deficient in sulfur for crops with high sulfur demands may be found.

Response of crops to addition of sulfur to Indiana soils

The final answer to our balance sheet in specific local areas is whether crops respond to sulfur as a fertilizer on these soils. Only preliminary field experiments have been conducted in Indiana to determine whether such crops as alfalfa and

[3] Ford, O. W., Purdue Agricultural Experiment Station. Personal Communication.

soybean respond to sulfur fertilization. Alfalfa grown on Culver fine sand near Culver, Indiana, failed to show response to sulfur applied at rates up to 900 pounds per acre. On Newton fine sandy loam, similar results were obtained with sulfur applications up to 450 pounds per acre. Where 900 pounds of sulfur per acre was applied, there was some indication of a depression in yield.

Greenhouse experiments were conducted on three other soil types to determine response of alfalfa to sulfur. Two-gallon crocks containing 7 kgm. of soil were used in these experiments. The results from four cuttings are summarized in table 5. Under these conditions, sulfur-deficiency symptoms were manifested in the untreated pots. The greatest response was shown on Hagerstown silt loam and Plainsfield fine sand. The 224-pound treatment gave about as good yields as the 900-pound treatment, indicating that this rate was adequate under existing conditions for these two soils. Though the responses to sulfur indicate an insufficiency of this nutrient, the following factors were different from normal field conditions: the cropping was much more intensive than occurs in the field, all other fertility factors were maintained at an optimum, and replenishment of sul-

TABLE 4

Estimates of annual sources and losses of sulfur in soils of Indiana

GAINS		LOSSES	
Source*	Amount	Source	Amount
	lb./A.		*lb./A.*
Sulfur brought down by precipitation	27	Crop removal (3 tons alfalfa)	17
Sulfur absorbed directly by soil	27	Leaching	37
Sulfur returned in fertilizers, residues, and manures	12	Erosion	6
Sulfur absorbed directly by plants	1	Total	60
Total	67		

* Sulfur contained in the soil may vary from 200 to 2,000 pounds per acre; but if organic matter is maintained this will continue to be a reserve with losses and additions cancelling.

TABLE 5

Yield from four cuttings of alfalfa grown in the greenhouse on three soil types treated with flowers of sulfur

SULFUR PER ACRE	ALFALFA YIELD PER POT*		
	Cincinnati silt loam	Hagerstown silt loam	Plainfield fine sand
lb.	*gm.*	*gm.*	*gm.*
0	25.0	15.3	37.5
56	27.4	29.1	41.9
224	29.0	30.3	46.0
896	31.6	31.9	46.5

* Each pot contained 7 kgm. soil on oven-dry basis.

fur from the atmosphere by precipitation was prevented. Maximum yields from these four cuttings in one year ranged as high as 8 to 10 tons per acre when calculated on a field basis; 4 tons per acre is considered a good annual yield under average Indiana field conditions.

SULFUR AS A SOIL AMENDMENT

As a soil amendment, sulfur may affect the availability of other nutrients in several ways, such as by lowering the pH, perhaps by ionic relationships when it forms the sulfate ion, and, as suggested in another paper (28), by serving as a reductant or electron donor.

Experiments were conducted to determine the effect of particle size on ability of sulfur to lower pH and increase the NH_4Ac-extractable manganese from a nearly neutral Maumee loam that is often deficient in manganese. To 200 gm. of soil, which had been placed in glass tumblers, was added 0.5 gm. of either ground or blown sulfur pellets. Three particle sizes, 14–20, 20–35, and 80 mesh, were used with the ground sulfur, and three, 14–20, 20–35, and 35 mesh, with the blown pellets. The 80-mesh ground sulfur was the most effective in lowering the pH and increasing the NH_4Ac-extractable manganese (fig. 1); the 35-mesh pellets were effective in lowering the pH, but did not bring so much manganese into solution.

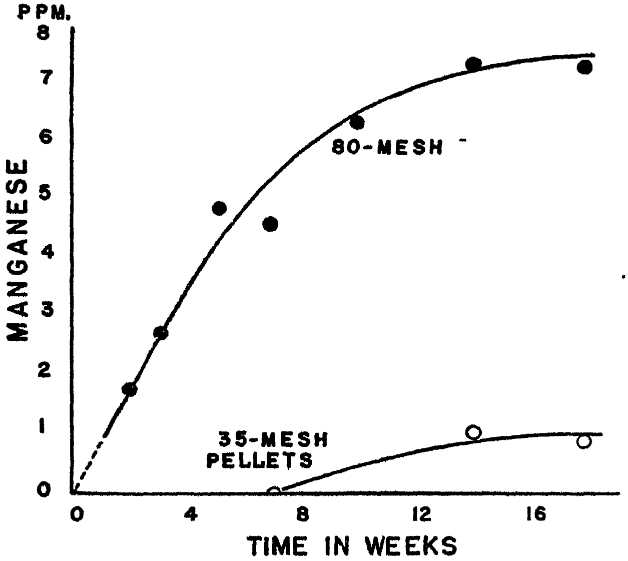

FIG. 1. EFFECT OF FINENESS OF SULFUR ON THE NH_4 AC-SOLUBLE MANGANESE OF MAUMEE LOAM

The 14- to 20-mesh sulfur failed to lower the soil pH to any marked degree. During the 18 weeks of the experiment, the pH was gradually reduced from 6.8 to 6.2. At no time was NH_4Ac-extractable manganese detectable with this treatment.

When equal particle sizes were compared, there was little difference in the action of the blown pellets and the ground sulfur. The inverse relation between the soil pH and the ammonium-acetate-extractable manganese is shown in figure 2. A marked change in pH and manganese occurred during the first 4 weeks. Then there was a tapering off in pH change; but the extractable manganese continued to increase rapidly for another 4-week period, which seems to indicate that some factor other than pH is also involved. This may be the reducing action of the sulfur (28).

Field experiments were conducted on a Maumee loam to study the effectiveness of sulfur of two sizes, 20–35 and 80-mesh. Three rates of these two materials were compared with soil applications of $MnCl_2$ for correcting manganese deficiency of soybeans. The treatments and chemical analysis are summarized in table 6.

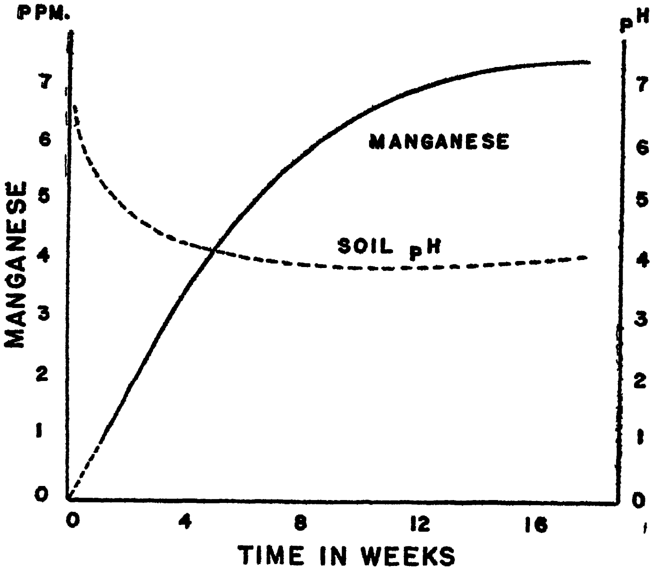

FIG. 2. Relationship Between Change in pH and NH_4 Ac-Soluble Manganese Following Treatment of 200 gm. of Maumee Loam With 0.5 gm. 80-Mesh Sulfur and Incubation at 25° C. and Optimum Moisture.

Increasing applications of sulfur resulted in an increased manganese content of the plant, and generally a decrease in the percentage total nitrogen. There was a decrease in pH with each additional increment of sulfur added. Consistently lower pH and higher NH_4Ac-soluble manganese values for each increment of sulfur were obtained with the 80-mesh sulfur than with the 20–35-mesh. A high negative correlation between soil pH and NH_4Ac-soluble manganese was found; the value of r was 0.854 (fig. 3). Between pH limits encountered in this experiment, the variation of soluble manganese with pH is linear. The regression of Y on X is given by the expression $\hat{Y} = 5.48 - 0.756X$. A good correlation exists between soil pH and the amount of manganese absorbed by the plant (fig. 4). The value of r in this case is -0.833. The regression equation is $\hat{Y} = 130 - 16.08X$. Likewise, the correlation between the NH_4Ac-soluble manganese in the soil and the manganese content of the plants is high (fig. 5). The correlation coefficient is $+0.818$.

The $MnCl_2$-treated plots showed considerable chlorosis during the early stages of soybean growth. Apparently this was before the roots had been able to forage sufficiently into the band of fertilizer. On the other hand, scarcely any chlorosis was observed in the early stages of growth on sulfur-treated plots receiving the 20–35-mesh sulfur, and no chlorosis was observed where the 80-mesh material was used.

TABLE 6

*Effect of amount and particle size of sulfur on ammonium-acetate-soluble manganese and soil reaction of Maumee loam; manganese content, and total nitrogen content of soybean plants grown on this soil in Pulaski County, Indiana, 1948**

TREATMENT PER ACRE	pH	NH_4Ac-SOLUBLE MN IN SOIL	MN CONTENT OF PLANT	TOTAL N CONTENT OF PLANT
		ppm.	*ppm.*	*per cent*
None	6.7	0.41	15.3	3.25
90 lb. $MnCl_2 \cdot 4H_2O$	6.7	0.52	20.1	3.28
384 lb. 20–35-mesh sulfur	6.6	0.54	20.0	3.20
768 lb. 20–35-mesh sulfur	6.4	0.62	21.8	3.23
1152 lb. 20–35-mesh sulfur	6.4	0.69	24.5	3.08
384 lb. 80-mesh sulfur	6.3	0.63	24.5	2.99
768 lb. 80-mesh sulfur	6.0	0.94	30.3	2.93
1152 lb. 80-mesh sulfur	5.7	1.29	35.8	2.97
Least significant difference at 5 per cent level	0.2	2.64	4.4	0.12

* All figures are averages of four replications.

Soil samples July 17 and plants sampled August 7.

Manganese and total nitrogen determinations were made on oven-dry plant material. All plots received a basic application of 1,000 pounds of 0–15–15 fertilizer broadcast, half plowed under and half disced in 10 days before planting.

Manganese chloride was mixed with quartz sand and drilled in a band about 2 inches to the side of seed with a hand distributor at planting time. Soil sampling for NH_4Ac-soluble manganese determination was done in this band on this treatment.

All sulfur treatments were mixed with the 0–15–15 fertilizer.

The yields from these treatments are summarized in table 7. They were all rather low because a drought terminated the growing season too early, and hence water as a limiting factor may have narrowed the differences. These results would lead one to suspect that the 384-pound application of sulfur may have been more than was needed, since the increase in yield with additional increments is small and statistically nonsignificant. The sulfur and the manganese chloride treatments proved equally effective in increasing the yield of soybeans.

The 1,152-pound treatment of 80-mesh sulfur resulted in an increase of more than 1 per cent in oil content. The oil content of the beans from this treatment was significantly higher than from the check, from the $MnCl_2$-treated plot, and from plots treated with 20–35-mesh sulfur.

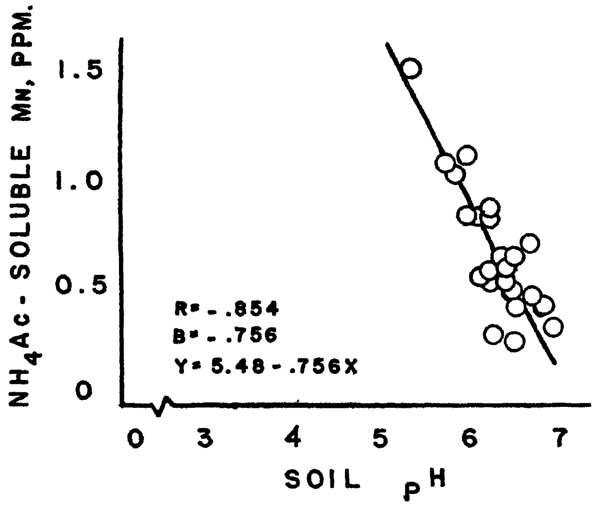

FIG. 3. RELATIONSHIP BETWEEN SOIL pH AND NH_4 AC-SOLUBLE MANGANESE IN MAUMEE FINE SANDY LOAM

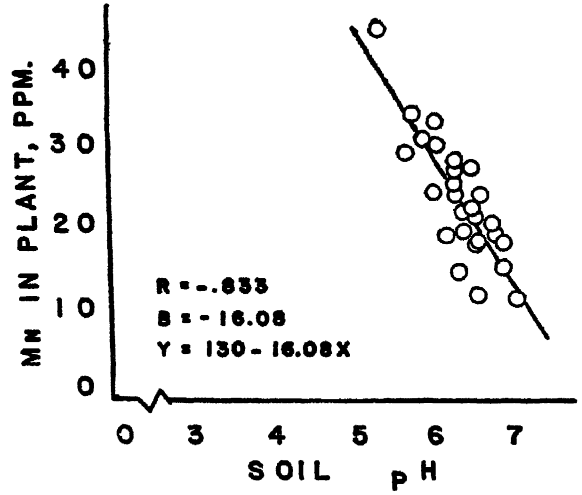

FIG. 4. RELATIONSHIP BETWEEN SOIL pH AND MANGANESE CONTENT OF OVEN-DRIED SOYBEAN PLANTS GROWN ON MAUMEE FINE SANDY LOAM

Use of sulfur for the correction of manganese deficiency is not new. The advantage of sulfur treatments over the use of manganese in annual application depends upon: first, whether there is an adequate supply of soil manganese to be released by the sulfur treatment; and second, the length of time that a sulfur treatment will control the deficiency. These factors are still being studied. The winter wheat crop on these experimental plots in 1949 gave responses similar to those obtained in 1948 with the soybeans.

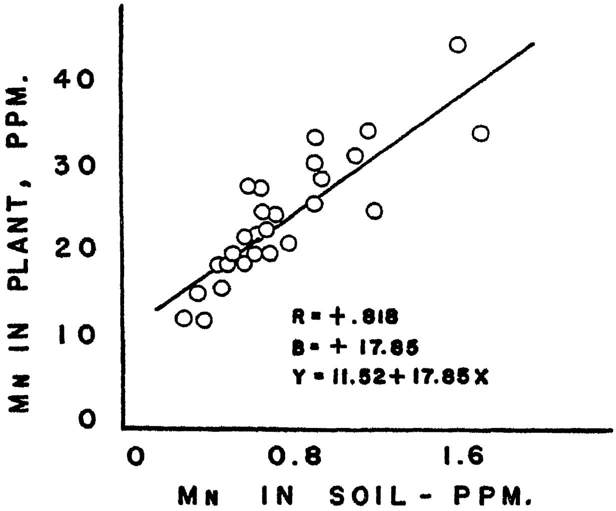

FIG. 5. RELATIONSHIP BETWEEN NH_4 AC-SOLUBLE SOIL MANGANESE AND THE MANGANESE CONTENT OF SOYBEAN PLANTS GROWN ON MAUMEE FINE SANDY LOAM

TABLE 7

Effect of sulfur treatments on yield and oil content of Richland soybeans grown on Maumee loam in 1948

TREATMENT	YIELD	OIL*
	bu./A.	*per cent*
None	16.2	17.98
$MnCl_2$	24.4	18.22
384 lb. 20–35-mesh sulfur	22.3	18.33
768 lb. 20–35-mesh sulfur	23.0	18.02
1152 lb. 20–35-mesh sulfur	24.5	18.31
384 lb. 80-mesh sulfur	25.4	18.62
768 lb. 80-mesh sulfur	25.0	18.54
1152 lb. 80-mesh sulfur	25.3	19.07
Least significant difference at 5 per cent level	3.8	0.65

* Oil content was determined by the agricultural chemistry department.

EFFECT OF SULFUR ON NUTRIENT VALUE OF TWO ALFALFA STRAINS

During alfalfa breeding experiments conducted at Purdue[4] in 1947, a strain of alfalfa, C-10, was found to have an unusually high methionine content. Another strain, C-3, was only average in methionine content. The behavior of these two strains when subjected to different levels of sulfur as sulfate was studied. The plants were obtained by clonal propagation and grown in sand culture. A complete nutrient solution, minus sulfur, was used. Sulfur was included in the following concentrations: 0, 1, 3, 9, 27, and 81 ppm. of sulfate. This experiment is reported in detail elsewhere (19, 29), but the principles involved seem to warrant presentation in this paper.

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[4] This research was under the supervision of H. R. Albrecht, who suggested the possibilities of this study.

TABLE 8

Effect of sulfate-ion concentration on yield of two strains of alfalfa grown in sand cultures in greenhouse

SO_4 CONCENTRATION	YIELD FROM 3 CUTTINGS*	
	C-3 (Low methionine)	C-10 (High methionine)
ppm.	*gm.*	*gm.*
0	9.5	7.3
1	16.2	11.3
3	19.1	16.5
9	30.6	26.7
27	32.6	27.5
81	30.9	28.5

* All yields are averages of three replications and are expressed in grams of oven-dry plant material per pot.

TABLE 9

Effect of sulfate-ion concentration in nutrient solution on methionine, cystine, total sulfur, and nitrogen content of two strains of alfalfa grown in greenhouse

First cutting, harvested Nov. 4, 1947

SO_4 ION CONCENTRATION IN SOLUTION	STRAIN	METHIONINE*	CYSTINE*	SULFUR*	NITROGEN*
ppm.		*mgm./gm. N*	*mgm./gm. N*	*per cent*	*per cent*
0	C-3	29.6	24.65	.121	3.45
1	C-3	39.0	28.60	.125	3.31
3	C-3	45.7	37.00	.160	3.04
9	C-3	47.2	53.10	.200	3.39
27	C-3	46.8	49.25	.208	3.25
81	C-3	48.7	55.25	.221	3.35
0	C-10	41.8	46.45	.129	3.66
1	C-10	40.4	45.45	.141	3.74
3	C-10	45.0	50.25	.153	3.50
9	C-10	47.4	60.05	.192	3.52
28	C-10	53.4	64.30	.224	3.50
81	C-10	49.5	62.85	.229	3.50

* Plant material from each of three replications were mixed in equal quantities, and analyses were made on the composited sample. All figures are averages of three to five determinations.

Though it is difficult to obtain significant differences with these small populations and only three replications, it is noteworthy that the C-3 strain gave greater yields at all concentrations of sulfur (table 8). At the higher concentrations, however, the differences in yield on a percentage basis were not great and likely were nonsignificant. The analytical results on the plant material (table 9) demonstrate the greater ability of the C-10 to produce higher quality forage. On a unit-weight basis, the C-10 produced forage richer in methionine than the C-3 at the lowest concentration of sulfur. The C-10 produced forage richer in cystine at all concentrations of sulfur. Since the sulfur content of the two strains was similar at any given concentration of sulfur in the nutrient solutions, the ability of the two strains to elaborate the sulfur into amino acids obviously is not determined by the rate of absorption of the sulfate anion, but rather is dependent on ability to convert the sulfate into organic combination after it has entered the plant system. Though the C-3 was lower than the C-10 in nitrogen content at all levels of sulfur, the relationship between sulfur and nitrogen does not lend itself to interpretation from these data.

The fact that plant performance is controlled by genetic and fertility factors demonstrates the need for common knowledge between the plant breeder and the soil fertility specialist. The plant breeder conducting yield tests on a soil deficient in sulfur might select, on the basis of yield alone, an alfalfa plant that would not be especially desirable, since it had demonstrated superior productivity only because it could tolerate a lower level of sulfur fertility by producing a forage inferior in nutritive quality. On the other hand, the soil fertility specialist might use a strain that was inferior in nutritive quality to determine whether the level of sulfur fertility was adequate.

SUMMARY

Studies on the sulfur balance of Indiana soils lead to the following conclusions:

The amount of sulfur brought down in 1 year in the precipitation varied between 20 and 127 pounds per acre, with an average of about 27 pounds when the figure for Gary, an industrial area, is omitted.

Direct absorption of sulfur by plants and its elaboration into organic constituents has been conclusively demonstrated.

The sulfur balance seems to indicate that under average conditions of crop production, the likelihood of sulfur deficiency is not great at present. This does not preclude, however, large local areas which may be deficient in sulfur for maximum crop yields.

Although field tests failed to show a response to sulfur fertilization, intensive cropping with alfalfa in the greenhouse brought about sulfur-deficiency symptoms and marked reductions in yield on several soils.

Use of sulfur as a soil amendment gave special promise in the manganese-deficient areas of northern Indiana.

Studies are reported which demonstrate the dependence of geneticists and soil fertility specialists upon each other to avoid erroneous conclusions in some phases of their work.

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RELATIONS OF MICROORGANISMS TO TRANSFORMATIONS OF SULFUR IN SOILS

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Sulfur is an essential element for all forms of life, for it is a common constituent of proteins, with the sulfur in the amino compounds cystine (or cysteine) and methionine. Furthermore, it is contained in many other important cell compounds, such as the vitamins thiamin and biotin.

With some microorganisms sulfur plays a role of particular importance, for with them it may be a specific hydrogen donor or acceptor. In the former case it serves either as a source of energy for cell development or as a reducing agent for CO_2 that is assimilated in a manner similar to that in green plants. When the sulfur compound acts as a specific hydrogen acceptor, the donor is the energy source.

Many of the microorganisms that transform sulfur and its compounds are active in soils. Some act on organic sulfur compounds, liberating the sulfur in inorganic forms. Others oxidize or reduce inorganic sulfur compounds. Although their reactions are diverse and various products are formed, incompletely oxidized sulfur materials do not generally accumulate in soils. The transformation of any one organism is masked by the reactions of others, and the material that accumulates is either the completely oxidized product sulfate, under aerobic conditions, or the reduced product sulfide, under anaerobic conditions. Organic compounds in the cells of microorganisms, in higher plants and animals that populate the soil, and in the inanimate matter undergoing decomposition account for the rest of the soil sulfur.

In humid regions most of the sulfur is in organic compounds. Rippel reported that in a field soil with 0.042 per cent total sulfur, 14 per cent was sulfate; in a forest soil with 0.058 per cent total sulfur, 10 per cent was sulfate; and in a compost soil with 0.126 per cent total sulfur, 21 per cent was sulfate (30). A fertile soil examined by Bertrand and Silberstein contained 0.52 per cent total sulfur, of which 21 per cent was sulfate (6). The total sulfur content of field soils is more commonly 0.01 to 0.05 per cent or 200 to 1,000 pounds per acre in humid regions, but it may be considerably higher in regions with deficient rainfall where salts accumulate. Lack of persistence of sulfate is due to the relatively high solubility of the salts. Sulfur of organic materials is transformed to sulfate during decomposition; similarly, nitrate is formed from the organic nitrogenous compounds. The microbial transformations involved in the breakdown of organic compounds to sulfate are more numerous, however, and a greater variety of microorganisms is concerned.

Organic sulfur in soils is important as a reservoir of the element for plant development. Sulfate is readily leached from soil, whereas the sulfur in organic compounds resists leaching and is gradually broken down to sulfate. It is generally assumed that higher plants obtain sulfur from soil as sulfate. Although sulfate may be the principal source of sulfur for plant development, it may not be the only source of the element. In a recent communication, Miller reported results showing that the amino acid methionine was absorbed by tomato and tobacco plants and that the sulfur was converted to sulfate as well as to diverse sulfur compounds in the plant (21). The plants grew with sulfur supplied only as methionine, which presumably satisfied all the sulfur requirements.

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Little is known about the sulfur constituents of soil. Determinations are generally confined to total sulfur and sulfate. Some years ago Shorey reported the occurrence of trithiobenzaldehyde in soil (32). He suggested that it might be produced by interaction between H_2S formed by microorganisms and benzaldehyde. A great variety of organic sulfur compounds is present in the soil organic matter as proteins and other compounds produced by higher plants, animals, and microorganisms. Among the inorganic sulfur compounds in addition to H_2S and sulfate that have been detected in soils are elemental sulfur, thiosulfate, tetrathionate, and other polythionates. Consideration of the reactions whereby organic and inorganic sulfur compounds are transformed by microorganisms leads one to believe that many sulfur compounds are produced in soil, but, because they are susceptible to decomposition, they do not accumulate and are not readily detected.

Among the principal compounds of biological origin containing sulfur are the amino acids cystine (disulfide), cysteine (hydrosulfide), methionine (methylated sulfur), taurine (sulfonic acid), ethereal sulfates, thiourea, glucosides, and alkaloids and in addition, vitamins such as thiamin (cyclic) and biotin (cyclic). The sulfur content of proteins varies from 0.2 to 2 per cent, that of some sulfur-containing glucosides as sinalbin and sinigrin from 8 to 16 per cent, of alkyl mustard oil 32 per cent, of taurine 25 per cent, of cystine 27 per cent, and of methionine 21 per cent.

It has been reported that nodulation of legumes is poor in cases of sulfur deficiency, and from this it might seem that deficiency of sulfur affects the process of nitrogen fixation directly. Recent results of Anderson and Spencer tend to disprove this. These workers reported on the condition of plants grown on soils deficient in molybdenum and sulfur (1). Clover on soil deficient in sulfur grew poorly, showed little response to added nitrogen, and had very few nodules and these were small. Addition of sulfate resulted in increase in nitrogen fixation and in growth. It was concluded that although deficiency of sulfur or molybdenum inhibited fixation of nitrogen, the effects of the two elements were not alike. Whereas molybdenum was needed for the process of nitrogen fixation, sulfur appeared to exert its effect on the nitrogen metabolism of the plant, that is, the actual utilization of the nitrogen compounds and incorporation of the nitrogen in proteins and other compounds. This indicates that the effects of sulfur on plant development are similar with legumes and nonlegumes (26).

In organic compounds, sulfur more closely resembles nitrogen than other elements. Furthermore, the oxidation and reduction reactions of microorganisms involving nitrogen and sulfur show many similarities. There is no simple sulfur cycle in soil. Only in a general way can one refer to the sulfur cycle. When all of the many microbial transformations of sulfur are considered one finds an intertwined network of reactions.

This report is concerned principally with the kinds of transformations of inorganic and organic compounds of sulfur as well as elemental sulfur brought about by microorganisms. Most of the microorganisms referred to inhabit soils. Some are not typical soil organisms, but it is possible that the reactions they effect can be performed by some soil organisms. To characterize the transformations accurately, most of the studies have been carried out in laboratory media rather than in soil.

TRANSFORMATION OF INORGANIC SULFUR COMPOUNDS

Oxidations

More precise information is available on the microbial transformation of the organic compounds. Conspicuous members of inorganic sulfur compounds than of the bacteria that transform inorganic sulfur compounds are the autotrophic organisms that belong to the group characterized by their ability to grow on substrates free of organic matter and by their ability to make use of CO_2 as their sole source of carbon.

Among the bacteria that bring about oxidation reactions are those that oxidize sulfide, elemental sulfur, and thiosulfate. In soils, it is unlikely that microbial oxidation of sulfide is important, for the sulfide is so unstable in the soil environment that it becomes oxidized with the liberation of sulfur by strictly chemical reactions. This commonly occurs when waterlogged soils in which sulfide has accumulated become drained, allowing penetration of oxygen. The bacteria principally concerned in the oxidation of H_2S are water organisms, among which are certain colorless filamentous bacteria such as *Beggiatoa* and *Thiothrix* and the purple and green photosynthetic bacteria such as *Chromatium* and *Chlorobium*.

Elemental sulfur undergoes relatively rapid oxidation by various microorganisms. Of particular importance is *Thiobacillus thiooxidans,* which not only oxidizes elemental sulfur but tolerates exceedingly high acidity that frequently develops in soils where sulfur is thus transformed. Jensen found that a sandy soil from a dried marsh had a pH of 2.2 (19). The acidity was found to be due to sulfuric acid produced by the oxidation of sulfur. A pH of 2.4 was reported by Drewes for a moor soil, and the acidity was also ascribed to development of *T. thiooxidans* (11). In a sandy or gravelly drained area of the Zuider Zee, Harmsen reported exceedingly high acidity (in certain cases even a negative pH) caused by sulfur oxidation by the same organism (17). *T. thiooxidans* has also been implicated in corrosion of iron and concrete. It has also been reputed to produce the sulfuric acid that makes the waters of coal mines very acid (9, 18, 20). As a result of the acid, the waters become heavily laden with ferrous iron, which causes troublesome pollution of streams and rivers. The amount of sulfuric acid pouring into the Ohio River and its tributaries from the coal mines has been estimated to be equivalent to 3,000,000 tons of concentrated sulfuric acid per year.

It may be recalled that some years ago a plan was proposed by Lipman whereby soluble phosphates could be made from superphosphate on the farm. According to the proposal, composts were to be prepared of soil, rock phosphate and sulfur. The bacterium *T. thiooxidans* would oxidize the sulfur to sulfuric acid, which would react with the rock phosphate and produce monocalcium and dicalcium phosphates. The transformation is readily brought about, but the process has never been widely used.

On occasion, elemental sulfur is added to soil to increase acidity, as with potato soils for control of potato scab, or in reclamation of alkali soils. It may also be used in soils deficient in sulfur. It has been proposed that sulfur inoculated with *T. thiooxidans* be used in these cases. There is considerable evidence that sulfur is oxidized more rapidly in soils containing an abundance of these bacteria than in soils from which the bacteria are absent, but the conditions under which the bacteria are held in the inoculated sulfur are such that it is doubtful that any benefit results from the inoculum. The bacteria die rapidly when desiccated, and they live but a short time in dry sulfur.

Generally it is impossible to recover *T. thiooxidans* from cultivated soils that have received no additions of elemental sulfur. Sulfur treatment may result in appearance of the bacterium, however, as shown by Sijderius (33). He was unable to obtain the bacterium from an untreated field soil. Five weeks after sterile sulfur had been added to the soil, the pH had dropped to 4.5; in 7 months it had dropped to between 3.0 and 3.5. After this prolonged period *T. thiooxidans* was readily obtained in laboratory media inoculated with the soil. It was concluded that this sulfur-oxidizing bacterium is not uncommon in soils, but that it is present in very small numbers. The bacterium develops in soil enriched with sulfur and, as a result of the increased abundance of cells, it can be readily recovered from the soil.

Sulfur is oxidized, but slowly, by another sulfur bacterium, *T. thioparus*, whereby it is transformed to sulfate (38). Guittonneau observed that various microorganisms including certain bacteria, actinomycetes, and filamentous fungi were also able to attack sulfur with the formation of thiosulfate (14). These heterotrophic bacteria required organic matter for development. Guittonneau and Keilling found that these heterotrophic microorganisms transformed elemental sulfur to thiosulfate and polythionates, particularly tetrathionate (15). These products were recovered from sulfur-treated soils.

Even though sulfur in soil may be oxidized more rapidly by *T. thiooxidans* than by the heterotrophic microorganisms, no difficulty should be encountered in obtaining oxidation of sulfur in absence of this organism in fertile soils, for such soils should contain an abundance of microorganisms that will oxidize sulfur when provided with decomposable organic matter.

Thiosulfate is oxidized to sulfate by the autotrophic bacterium *T. thiooxidans*. The sulfur of thiosulfate is transformed to nearly equal portions of sulfate and elemental sulfur by another autotrophic bacterium, *T. thioparus*. An organism referred to as *T. novellus*, but more recently classified as *Micrococcus denitrificans* (33), is a facultative autotroph that oxidizes thiosulfate to sulfate (38). When growing on organic substances, various other microorganisms, including many species of the genus *Pseudomonas* and some actinomycetes and filamentous fungi, are able to transform thiosulfate to tetrathionates (37).

Polythionates are unstable, particularly at alkaline reactions, and they undergo decomposition to sulfur and sulfate by strictly chemical reactions. It has been reported that some polythionates may be oxidized to sulfate by *T. thioparus*.

Animal tissues also have enzymes that are able to bring about oxidations similar to those of some of the bacteria. Pirie found that some tissues were able to oxidize thiosulfate and tetrathionate to sulfate, the latter at a slower rate than the former (27).

Thiocyanate is toxic to many microorganisms, but for some it can serve as a source of either sulfur or nitrogen. Tanner (42) reported that 9 of 30 yeasts and related organisms produced sulfide from potassium thiocyanate. He also verified the observation of Neuberg and Welde (22) that thiosulfate was broken down to sulfide and sulfite by many yeasts. Armstrong (2) found that thiocyanate could be used as a source of sulfur by the fungi *Aspergillus niger*, *Penicillium glaucum*, and *Botrytis cinerea* but it was not so readily utilized as sulfate, thiosulfate, hydrosulfide, sulfite, or persulfate. Some sulfide was produced from thiosulfate and thiocyanate.

Beijerinck (5) noted that crude cultures from canal water or ditch mud produced an abundance of elemental sulfur in a solution medium containing no other organic substance than ammonium thiocyanate.

An organism given the name *Bacterium thiocyanoxidans* by Happold and Key (16) was believed to decompose ammonium thiocyanate to ammonium sulfate and carbon dioxide and to grow on the compound, using it as a source of both carbon and nitrogen. The culture was obtained from activated sludge that brought about rapid decomposition of the thiocyanate.

The reactions of most of the microorganisms so far mentioned are brought about aerobically. Oxidation of sulfur and thiosulfate to sulfate may also be effected anaerobically by an organism referred to as *T. denitrificans* which uses nitrate as the hydrogen acceptor, and by the purple sulfur bacteria that develop anaerobically.

Apparently, many microorganisms, particularly certain autotrophic bacteria, oxidize sulfur and thiosulfate to sulfate. Numerous heterotrophic microorganisms may also participate in reactions leading to the oxidation of these compounds to sulfate.

Reductions

The reactions whereby sulfur compounds are reduced are endothermal and consequently are effected almost exclusively by heterotrophic microorganisms that use organic materials as sources of energy. The reduction of sulfate and incompletely oxidized inorganic sulfur compounds with the formation of sulfide is not likely to be important in arable soils because this occurs under conditions where oxygen is excluded and anaerobic transformations predominate; nevertheless, sulfate reduction occurs in waterlogged soils. The transformation is of great interest microbiologically, for it is effected by a unique group of bacteria known as sulfate-reducing bacteria. With these organisms, sulfate is the principal hydrogen acceptor whereby they develop under anaerobic conditions, using organic materials or even H_2 as sources of energy. Black coloration of iron sulfides that characterize waterlogged soils is due to reduction of sulfate by these bacteria. They have been implicated in the anaerobic corrosion of steel and iron in soil and are responsible for the production of sulfide in such large amounts as to be destructive or obnoxious along coastal regions and at sea (39). There have been reports that sulfate is reduced by certain other microorganisms either to elemental sulfur or to sulfide. With some of these organisms, the amounts of sulfide thus produced may be too small to be of particular importance; in other cases, additional evidence is needed to establish the validity of the claims. An interesting case of reduction of sulfate by an organism other than the specific sulfate-reducing bacteria was reported by Birkinshaw, Findlay, and Webb (7). These workers observed reduction of sulfate to methyl mercaptan by the fungus *Schizophyllum commune*. It was believed that the sulfate was reduced to sulfide, which became methylated to form methyl mercaptan. This transformation is remarkable not only because sulfate reduction is unusual for fungi, but because the product was a methylated compound. Methylation of sulfur compounds is doubtless common among microorganisms as well as higher organisms such as green plants, for sulfate can satisfy all the sulfur requirements of many organisms, and methylated compounds such as methionine are produced from it. The transformation observed by Birkinshaw, Findlay, and Webb is different from such reactions, however, for the methylated compound accumulated in the medium and did not represent an assimilated compound. Challenger and Charlton verified these results and noted that dimethyl sulfide and some dimethyl disulfide were also present in the products (8). It was thought that dimethyl disulfide might be a product of oxidation of methyl mercaptan.

Incompletely oxidized sulfur compounds are much more susceptible to attack than is sulfate. Thiosulfate and elemental sulfur are reduced to sulfide not only by sulfate-reducing bacteria, but also by various other bacteria and by yeasts. Tarr reported formation of sulfide from thiosulfate by *Proteus vulgaris* (43). According to Tanner, various bacteria, particularly members of the genus *Pseudomonas*, produce sulfide from thiosulfate (41). Reduction was also effected by *Escherichia coli* (3). It may be recalled that a reduced product, elemental sulfur, resulted from the transformation of thiosulfate by *T. thioparus*.

Pollock, Knox, and Gell reported the reduction of tetrathionate to thiosulfate by certain intestinal bacteria (28, 29). Armstrong reported the production of sulfide by various fungi from thiosulfate, sulfite, and thiocyanate (2).

Elemental sulfur is susceptible to reduction to hydrogen sulfide by many microorganisms. In the case of sulfate-reducing bacteria, the elemental sulfur serves as the specific hydrogen acceptor, but with most of the other microorganisms that produce sulfide from sulfur and also from thiosulfate, the reactions belong in the category of the so-called phytochemical reactions (34). With sulfur there is a reaction between two molecules containing hydrosulfide groups with one atom of sulfur to produce disulfide and hydrogen sulfide.

TRANSFORMATION OF ORGANIC SULFUR COMPOUNDS

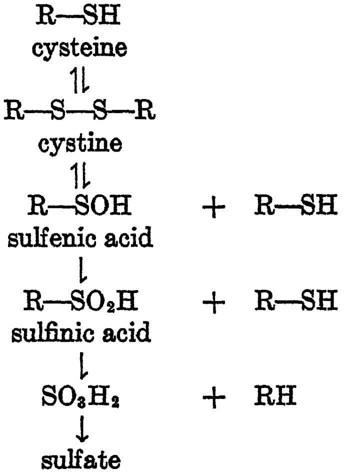
Decomposition of the organic compounds of sulfur is doubtless effected by many different types of reactions involving various microorganisms, for there are many organic sulfur compounds with different types of sulfur linkages. At present, there are only isolated reports of the reactions whereby the compounds are broken down with the release of inorganic sulfur. The information is too fragmentary to permit generalizations regarding the susceptibility of the sulfur in different linkages to decomposition or the nature of the inorganic sulfur compounds that are likely to be released from these compounds. It has long been known that sulfide can be produced by microbial decomposition of organic sulfur compounds, and the opinion is frequently expressed that sulfide is the most important if not the sole product of these transformations. Although sulfide may be formed when decomposition takes place under anaerobic conditions, it is not always a product under aerobic conditions. Other products than sulfide may indeed be more commonly produced under aerobic conditions, irrespective of the sulfur grouping in the organic compounds.

Much of the information on the breakdown of the organic sulfur compounds has been provided by studies of animal metabolism, but incorrect conclusions may be reached from drawing analogies between the reactions effected by animal tissues and microorganisms. Inorganic sulfate and taurine are two of the principal end products of sulfur metabolism in animals, but numerous other compounds are excreted, including ethereal sulfates and sulfonates (12, 35).

In studies of animal metabolism it was found that similar products are formed from both cystine and methionine. It therefore seems likely that methionine can be changed to cystine, thus explaining the similarity in final products. With certain microorganisms the same products are not obtained from cystine as from methionine. This suggests that with the organisms that were studied, at least, methionine did not pass through cystine during its breakdown. Other differences between transformations brought about by higher animals and microorganisms are to be noted in the decomposition of sulfonates. These resist attack by animal tissues, whereas compounds such as taurine and ethereal sulfates are decomposed by various microorganisms with release of sulfate. Neuberg and Kurono (23) and Neuberg (24) obtained an enzyme preparation from the fungus *Aspergillus oryzae* and from tissues of certain animals that hydrolyzed ethereal sulfates such as phenol sulfate. A similar transformation by some bacteria of the genus *Pseudomonas* was noted by Tankó (40). The sulfatase that attacked phenolsulfate differed from the enzyme that hydrolyzed chondroitinsulfuric acid. A similar bacterial enzyme was obtained by Neuberg and Cahill (25).

The decomposition of cystine has probably received more consideration than that of any other organic sulfur compound. In 1912 Sasaki and Otsuka reported that H_2S was liberated from cystine by bacteria (31). Tarr obtained H_2S from cystine, cysteine, and glutathione kept under anaerobic conditions with washed cells of *Pr. vulgaris* and *Serratia marcescens* (43). Sulfide was also produced from cysteine by *E. coli, Clostridium sporogenes, P. aeruginosa, B. subtilis,* and *Alcaligenes faecalis.* Both aerobic and anaerobic bacteria were therefore found to have the capacity to form sulfide from cystine when kept under anaerobic conditions. An enzyme able to liberate H_2S from cysteine was obtained by Desnuelle and Fromageot (10). This proved to be an adaptive enzyme.

An entirely different transformation was described by Barber and Burrows (4). These workers obtained from garden soil a bacterium, which they named *Achromobacter cystinovorum* and which transformed the cystine sulfur quantitatively to elemental sulfur. Sulfate was also obtained as a product of cystine decomposition by *Aspergillus niger* in experiments by Garreau (13). A similar transformation was noted by Pirie for animal tissues (27). In the transformation of wool by *Microsporum gypseum,* sulfate was also formed. Stahl *et al.* reported that when the keratin molecule that contains cystine was attacked by this fungus there was at first liberation of cystine, which underwent further breakdown to sulfate (36). Virtually all of the cystine sulfur was thus transformed. The following scheme was proposed to indicate the course of the transformation:



$$\begin{array}{ccc}
\text{R—SH} & & \\
\text{cysteine} & & \\
\rightleftharpoons & & \\
\text{R—S—S—R} & & \\
\text{cystine} & & \\
\rightleftharpoons & & \\
\text{R—SOH} & + & \text{R—SH} \\
\text{sulfenic acid} & & \\
\downarrow & & \\
\text{R—SO}_2\text{H} & + & \text{R—SH} \\
\text{sulfinic acid} & & \\
\downarrow & & \\
\text{SO}_3\text{H}_2 & + & \text{RH} \\
\downarrow & & \\
\text{sulfate} & &
\end{array}$$

The transformation of methionine by microorganisms appears to be different from that of cystine. Bacteria that released H_2S from cystine failed to produce sulfide from methionine (43). Challenger and Charlton obtained methyl mercaptan and dimethyl sulfide from methionine by action of *Scopulariopsis brevicaulis* (8). This fungus was able to transform various alkyl disulfides to alkyl mercaptans and methyl alkyl sulfides ($R—S—S—R \rightarrow R—SH + R - SCH_3$). It was also able to methylate mercaptans. Fission of the disulfide linkage of the simple aliphatic disulfides by this fungus was found to be a general reaction. Methyl mercaptan was obtained as a product of decomposition of methionine by the fungi *M. gypseum, S. brevicaulis* and *A. niger*, according to Stahl *et al.* (36).

Some results obtained from studies of organic sulfur compounds in the laboratories of the New Jersey Agricultural Experiment Station are similar to those already reported.[2] All of the decomposition studies were carried out under aerobic conditions. It has been found, for example, that in the decomposition of cystine, the inorganic products of decomposition are different with different organisms. With certain fungi, sulfate was the principal end product; with bacterial cultures, incompletely oxidized inorganic sulfur compounds as well as sulfate were produced. Although considerable elemental sulfur was formed, the transformation differed from the one discussed by Barber and Burrows (4) where the cystine sulfur was quantitatively changed to elemental sulfur.

As has been reported by others, methionine is less susceptible to attack than cystine. With certain bacteria, the products of decomposition were volatile and disappeared from the culture medium. It is probable that these bacterial products are similar to those formed by the fungus cultures of Challenger and Charlton (8) and Birkinshaw *et al.* (7), who found methyl mercaptan and dimethyl sulfide. Small amounts of some incompletely oxidized sulfur compounds, possibly thiosulfate, polythionates, or sulfide, were produced from methionine by certain actinomycetes.

Cystine and methionine added to soil and kept under conditions favorable for microbial development underwent relatively rapid decomposition with production of sulfate. The following compounds also decomposed more or less rapidly in soil: thiamine, taurine, sodium taurocholate, sodium formaldehyde sulfoxylate, sulfosalicylic acid, potassium ethyl xanthate, phenylthiourea, and thiourea. There was little or no decomposition of sulfonamides, long-chain sulfonates, sulfanilic acid, mercaptoethanol, or sodium diethyl dithiocarbamate during a period of several weeks. Decomposability of the various compounds did not seem to be related to any one or more types of sulfur linkages. Cystine is a disulfide, methionine is a thio-ether, thiamine has a thiazole ring, and taurine is a sulfonic acid. Decomposability is apparently associated with other portions of the molecule as well as the sulfur group.

CONCLUSIONS

This cursory review of the transformations of sulfur materials likely to occur in soils indicates that microorganisms participate in many reactions involving sulfur compounds. Inorganic compounds are oxidized and reduced and a variety of products are formed by these reactions as well as those concerned with the transformation of organic sulfur compounds. The liberation of sulfur from organic compounds provides sulfate, which may be used by the growing plant.

Just as with the breakdown of protein nitrogen to nitrate, the transformation of organic sulfur to sulfate tends to increase soil acidity. The most pronounced accumulation of acid by microorganisms that transform sulfur is not brought about in this way, however, but by the oxidation of sulfides that have accumulated in soils during a period when these were waterlogged and conditions were anaerobic and when considerable amounts of sulfate were introduced.

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[2] L. R. Frederick and William Segal participated in these studies carried out in the department of microbiology.

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SULFUR FUNGICIDES IN FRUIT PRODUCTION

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The purpose of this brief presentation is to discuss the use of sulfur fungicides in the production of the deciduous tree fruits. The viewpoint offered is that of a plant pathologist, not that of a chemist. Subjects for consideration include the character and types of materials available, the requirements of an acceptable fruit fungicide, the relation of sulfur to these demands, and the present and prospective position of sulfur as a fruit fungicide.

MATERIALS AVAILABLE

Sulfur is the most widely utilized fungicide in deciduous fruit production today, being utilized as the free element and in an aqueous calcium polysulfide solution. Elemental sulfur fungicides offered the grower include the flotation pastes, wet-milled paste, various dry-milled wettable powders, Grinrod process sulfur, and bentonite-sulfur blends. The discussion presented here is concerned primarily with the elemental sulfur fungicides rather than with the combined sulfur materials, of which liquid and dry lime-sulfur are the most important.

Typically, the elemental sulfur as offered to the trade is a finely milled powder with conditioning, wetting, and dispersing additives. The paste materials contain varying amounts of water, and because of their wet character, a minimum of additives. All products disperse readily in water to produce suspensions, the flocculent character of which varies with the individual product and the conditions of its use.

The fungicidal action of sulfur is manifest in the form of hydrogen sulfide, which is evolved through an interaction between the sulfur vapor and living fungal tissue. The natural physiological response of the fungus in a sulfur-vapor-bearing atmosphere serves to destroy the fungus.

The fungicidal effectiveness of elemental sulfur is correlated with the fineness of the individual sulfur particles. The importance of small particle size in the elemental sulfurs has been recognized for years, and much attention has been given to the development of fractionation methods and subsieve-size analysis. The fineness of the sulfur products available today generally reflects a recognition of the necessity of producing a finely divided product. Other things being equal, it might be assumed that the smaller the particle of sulfur the better, and to a considerable degree this is true. Other factors, however, enter into the picture and must be considered. Such factors include the ability of the product to deposit an amount of sulfur adequate in relation to surface area, the resistance of the deposit to weathering, and the agglomerating tendency of the product. The colloidal sulfur products which were used experimentally some years ago represented the ultimate extension of striving for fineness. Although the initial effectiveness of colloidal sulfur is high, the products were conspicuous failures because of their inability to deposit a consequential amount of sulfur, and that which was deposited did not persist long. A minimum size particle consistent with the physical requirements of deposit and retention is to be desired. This will normally fall in the 5 μ and below range. The dry products should be adequately conditioned and wet readily, yet be adjusted so they will deposit a maximum amount of suspended matter with a minimum of run-off. Pastes should be readily dispersible in water and possess a reasonable storage life without deterioration of physical condition. Resistance to freezing damage is desirable but not wholly necessary. Dustiness in the dry wettable products is a highly objectionable character because of the skin and eye irritation that many persons experience in mixing the product. More complaints are received on this property of the wettable sulfurs than from any other cause, and more than a few fruit growers avoid the dry sulfur fungicides because of the objections of the men to using it.

REQUIREMENTS OF A FRUIT FUNGICIDE

The important position of sulfur as a fruit fungicide developed as a natural consequence of the ability of the material to fulfill the three primary requisites of a fruit fungicide: First, *the fruit fungicide must be effective* in the control of diseases which affect the fruits in question, and against which the fungicide is directed. This is not to say that it must control all diseases which may afflict the crop, but it must be effective against the major disease or diseases for which control measures are necessary. Second, *it must be safe* to fruit and foliage, causing a minimal amount of injury. The object is the prevention of disease with preservation of fruit finish and foliage. Finally, *it must be compatible* with those insecticides and additives which are necessary to provide complete protection of the fruit. The acceptance and continued use of any fungicide must rest upon these three requirements. Failure to meet any of the requirements will cause a material to be discarded or severely restrict its usefulness. A case in point is the highly alkaline copper sprays which are not satisfactorily compatible with many of the new organic insecticides, although they still meet the first two requirements. Spraying is not wholly a matter of disease control, and where incompatibilities arise, choice for retention between materials will rest upon the relative importance of the tasks they have to perform and the availability of an alternative material. Secondary considerations include cost, convenience, and agreeableness in use, residues, and adaptability to special or unique situations. The several requirements and considerations noted are elaborated upon more fully in the discussion following.

SULFUR AS A FUNGICIDE

Sulfur fungicides are used on apples primarily for control of apple scab and on the stone fruits for control of brown rot. Sulfur is an effective protectant against both diseases. The elemental form is of limited usefulness as an eradicant of scab, whereas the value of liquid lime-sulfur as an early infection eradicant of apple scab has long been recognized and frequently utilized. Infection eradicants are of little use in brown rot control, and they are not used as the method-of-choice in any fruit disease control program.

The scab fungus overwinters in a saprophytic phase on the fallen and diseased leaves of the previous season. Ascospores are produced in these leaves and mature with the renewal of growth in spring. The mature spores are discharged during rains at this time and infect the new growth under favorable temperature and humidity conditions. Ascospores are discharged for only a limited time, and any subsequent development of scab must come from spores produced on these primary or initial infections. The key to the control of apple scab is prevention of early season primary infection, and this can be most economically accomplished through maintainance of a protective covering of sulfur during this critical period. The only other early season infections of major importance on the apple are the rusts, which have the red cedar as an alternate host. Apple varieties vary widely in their susceptibility to the rust diseases, and protection is provided only where a susceptible variety is grown in proximity to the red cedar. Sulfur is not adequately effective against the rust diseases, but fortunately it is fully compatible with the ferbam fungicides (ferric dimethyl dithiocarbamate) which are highly effective against the cedar rusts. A combination of elemental sulfur and a ferbam fungicide is effective against both scab and rust and is less expensive than an effective dosage of the organic fungicide alone. The early season use of sulfur usually provides adequate protection against occasional minor early season infections, but here again sulfur may be combined with an organic fungicide for broader protection.

Brown rot attacks and destroys peaches, cherries, and plums, both in the orchard and in market channels. Although brown rot causes its major loss through the rotting of mature fruit late in the season, early control measures are necessary with this disease too. The first appearance of brown rot is in the form of blossom blight. Some of these blighted blossoms and infected twigs persist through the summer and serve as a source of inoculum for fruit infection. The early development of brown-rot blossom infection of the peach is thus correlated with subsequent late season fruit infection. Protection against the blossom-blight phase of brown rot is commonly provided by a sulfur fungicide. Liquid lime-sulfur is most often used at this time, although the wettable sulfurs may be employed and are almost universally used on peaches following fruit set and until harvest.

The brown-rot fungus is susceptible to sulfur, and its spores are commonly employed as a test organism in the laboratory screening of fungicides. Sulfur is particularly well adapted to use on the peach, since it provides protection against both brown rot and peach scab, the two important fungus diseases that attack the peach during the growing season, and it is compatible with the necessary insecticides. Sulfur leaves a nontoxic and inconspicuous residue, an important consideration on a fruit from which residue removal is limited to brushing.

The sulfur fungicides are acceptably safe for use on both the pome and stone fruits during the season when their use in indicated. Injury from sulfur most commonly occurs when temperatures are high and humidity is low. Serious scald-ing of apple fruit and foliage may occur under these conditions, although such conditions do not occur frequently early in the season when sulfur is normally used. Although sulfur is used throughout the summer on the peach, the fruit seldom scalds if the tree is in normal foliage. The pubescence of the peach holds sulfur residues well and probably also serves to some extent as a protection against too close a contact between the fungicide and the surface of the fruit.

With the possible exception of one or two early sprays, fungicides are not used alone in a fruit protection spray program. Insects as well as diseases must be controlled; therefore, spray mixtures containing several materials are employed as a matter of necessity. Under these conditions the compatibility of the component pesticides assumes major importance. The various materials employed must retain their effectiveness in such combinations, must remain safe to fruit and foliage, and should not create physical difficulties in application. The elemental sulfurs meet the compatibility requirements as outlined with respect to the majority of the newer organic insecticides employed in fruit production. The principal insecticides employed in tree fruit production include DDT, parathion, benzene hexachloride, DDD, and lead arsenate. Less frequently used materials include the dinitro compounds, TEPP and HETP, chlordan, toxaphene, nicotine sulfate, and summer oil. The elemental sulfur fungicides are compatible with all of these materials except the dinitro compounds and summer oil. Sulfur is not safely compatible with either material, in spray suspension or as an adherent residue to which the insecticide may be applied within a few weeks. Difficulty is seldom encountered when the order of application is reversed. Sulfur fungicides must be used with caution in hot weather to avoid excessive residues and consequent sulfur scorch or scald. Application of a summer dinitro acaricide is particularly dangerous under such circumstances. The dangerous nature of sulfur-oil combinations has been recognized for years, but the problem has arisen less frequently as a complicating consideration following the introduction and use of the synthetic organic insecticides, which have much reduced the need for applications of summer oil on fruit. The problem of intercompatibility between the wetting and dispersing agents used in formulating the proprietary sulfur fungicides and organic insecticides occasionally arises to complicate spray operations, the suspended material curding or "greasing" out. Perhaps the greatest trouble has been experienced when mixing paste sulfurs with insecticide solutions that contain an emulsifying agent. This may be further complicated by the water supply itself.

The methods of pesticide application are presently undergoing change. So far as tree fruit production is concerned, the use of concentrate sprays is the most important development. The ability of a fungicide to lend itself to this method of application, in which sharply reduced volumes of more concentrated suspensions and solutions are applied with special equipment, is of major importance. The finer elemental sulfur fungicides have proved well adapted to concentrate application and are being commonly employed where this method of pesticide application has been adopted. Higher sulfur deposits have been obtained through concentrate application than in conventional practice, and no basic change in the formulation of the wettable sulfurs appears necessary to adapt them to concentrate application.

In both conventional and concentrate spray practice, the demand continues for more uniformly fine products, materials less objectionable to handle and more effective as fungicides. The sulfur fungicides tend to be lacking in desirable adhesive character, and frequent applications are necessary. The rapid growth of fruit trees in spring in itself requires frequent spraying to maintain coverage of new growth, but unfortunately some products are not sufficiently adhesive to provide protection through even this short period if there is much rainfall.

Sulfur fungicides interfere to some degree with the normal physiological functioning of the leaves, reducing their rate of carbon dioxide assimilation. Lime-sulfur is the greatest offender in this respect, and the curtailed use of the material is in large measure due to this action. The elemental sulfurs produce the same effect but to a considerably lesser degree. There is, nevertheless some tendency to restrict the use of those products for this reason, together with a feeling that too much sulfur may injure fruit finish.

The existence of allotropic forms of sulfur has long been recognized, but the possible role of such forms in fungicidal practice has received little attention. The high degree of effectiveness of liquid lime-sulfur as a fungicide has been tentatively attributed in part to the fact that the sulfur was deposited as an amorphous allotrope upon decomposition, although this does not seem to have been fully confirmed. Recent investigations have demonstrated a CS_2-insoluble amorphous allotrope to have a far higher degree of fungicidal effectiveness than the normal rhombic form of approximately the same particle size. Attempts have been made to utilize this character of the μ allotrope through precipitation of lime-sulfur with weak organic acids, but without marked success to date. One proprietary product is reputedly produced with a high percentage of the amorphous form, but judged by its performance in the orchard, the allotrope does not persist as a stable form.

CONCLUSIONS

Sulfur has long been, and promises to continue as an important fungicide in the deciduous fruit industry. It is particularly well adapted to use early in the season when temperatures are relatively low and the humidity is high. The inert and insoluble character of the sulfur particles makes the sulfur fungicides generally safe in spray mixtures and under conditions of prolonged wetting. They are not safe for use on the pome fruits during hot weather, nor are they adequately effective against the fruit infections which develop during the later season. They are generally safe and preferred for use on the peach throughout the season, and are used on other stone fruits to aid in brown-rot control although they are inadequate for foliage infections such as cherry leaf spot. They are generally compatible with the copper and organic fungicides and may be used in such mixtures to broaden the fungicidal protection afforded. The sulfur fungicides are among the least expensive of materials the grower uses and are convenient to use.

The prominent position of sulfur as a fruit fungicide was established almost coincident with the development of protective disease control practices in the fruit industry. The position of sulfur as a fungicide in fruit production remains of primary importance today despite the development and introduction of many new organic fungicides. Although the whole insect and disease control situation continues to undergo numerous and extensive changes, sulfur has continued to fit into a complete program. The position of sulfur as a fruit fungicide does not appear to be seriously threatened in the near future.

EFFECT OF SOIL ACIDIFICATION ON SOME CHEMICAL PROPERTIES OF A SOIL AND THE PLANTS GROWN THEREON

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In recent years several reports have been published (4, 5, 6, 7) which suggest that crop growth on alkaline soils can be improved by acidifying the soils. A primary argument of those who advocate acidification is that such a program will correct in plants grown thereon certain nutritional disorders which appear to be associated with the alkaline medium. Another report (1) indicates that nutrient uptake by plants is far greater when the soil is acid than when it is neutral and that in some cases this increased uptake reflects itself in increased crop yield.

Since many of the crops in California are grown on alkaline soils, a long-term investigation involving field and laboratory studies to determine the value of an acidification program for alkaline soils was undertaken a few years ago by the University of California Citrus Experiment Station. The information obtained from these studies indicates that the consequences of acidifying an alkaline soil are by no means so well defined as those resulting from the liming of an acid soil. A thorough understanding of the effect of acidification on the chemical, physical, and biological properties of the soil must be obtained before a general statement can be made about the value of an acidification program for alkaline soils.

The chemical data pertaining to soil and plants which are presented in this paper are fairly typical of those obtained in soil acidification studies. The data on plant growth are indicative of the variation in response which can be expected when a variety of crops are grown on an acidified, alkaline soil.

MATERIALS AND METHODS

An exploratory experiment involving a single soil and three treatment series, each acidified to four levels of pH with sulfuric acid, was set up to determine the influence of a change in soil reaction and chemical composition on the growth and mineral content of two widely different plants. The soil used in this investigation is classified as Ramona sandy loam, is noncalcareous, and was obtained from the surface foot of an unfertilized dry-farm grain field on the Citrus Experiment Station grounds. A buffer curve was made for the soil and served as the basis for the quantities of acid used in adjusting the pH of the soil to the desired levels. The pH of the unacidified soil as determined on a 1:2.5 soil-water suspension is 7.30. The pH of the treated soil at the time of planting appears in table 1.

The three-treatment series were set up in 8-inch clay pots, and each treatment was replicated three times. The first treatment series consisted of the unacidified soil and soil which had been adjusted in batch quantities to approximately pH 6.0, 5.0, 4.0, and 3.0. The second treatment series was identical to the first series except that treble superphosphate was added to each pot at the rate of 200 pounds of P_2O_5 per acre. Untreated tap water of pH 8.0 was used to irrigate all pots in treatment series 1 and 2. In the third treatment series, four sets of three pots were filled with untreated soil. The plants grown in these four sets of pots were then irrigated with water adjusted to pH 6.0, 5.0, 4.0, and 3.0, respectively.

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[1] Paper No. 635, University of California Citrus Experiment Station, Riverside, California.

Two successive crops, first alfalfa and then 1-year-old sweet orange seedlings, were grown in the soil in each pot. No nutrients other than those specified in the treatments were added to the pots while the alfalfa was growing. Subsequently, nitrogen as calcium nitrate was added periodically to all pots to main a healthy growth of the citrus seedlings. The alfalfa was harvested at full bloom by pulling the plants up by the roots while the soil was wet. The citrus seedlings were harvested in a similar fashion after 8 months of growth. In each case the top and roots were separated, washed in tap water, then rinsed in distilled water, and dried to constant weight in an oven regulated at 50° C. Yields are recorded on the basis of the 50° C. oven-dry weight.

TABLE 1

Some chemical properties of an acidified Ramona sandy loam at planting time

TREATMENT	pH OF 1:2.5 SOIL-WATER SUSPENSION	EXCHANGEABLE BASES				WATER-SOLUBLE BASES				CON-DUC-TIVITY K × 10^3	H_2O-SOLU-BLE PO_4	H_2O-SOLU-BLE Mn
		Ca	Mg	Na	K	Ca	Mg	Na	K			
		*me.**	*me.*	*me.*	*me.*	*me.*	*me.*	*me.*	*me.*	*mmhos/cm.*	*ppm.*	*ppm.*
pH 7.0 soil†	7.30	4.98	1.03	0.07	0.27	1.01	0.26	0.16	0.25	0.14	1.62	—
pH 6.0 soil	6.30	4.94	1.03	0.07	0.27	1.31	0.40	0.16	0.25	0.22	1.92	—
pH 5.0 soil	5.60	4.60	0.88	0.06	0.27	1.70	0.60	0.15	0.25	0.34	2.62	tr.
pH 4.0 soil	4.70	4.14	0.60	0.06	0.23	2.07	0.99	0.15	0.30	0.53	4.05	9.0
pH 3.0 soil	3.83	3.20	0.26	0.06	0.14	3.00	1.36	0.15	0.42	0.77	4.05	29.0

* me. in this table = per 100 gm. soil.

† Untreated soil.

Chemical analyses of the soil prior to and after cropping are reported on an air-dry weight basis, whereas the plant analyses are reported on a 105° C. oven-dry weight basis. Exchangeable cations were determined on a neutral, normal ammonium acetate extract of the soil after the water-soluble salts were removed from the soil by leaching. Conductivity, water-soluble phosphorus, and manganese were determined on a 1:5 soil-water extract after 1 hour's shaking. The pH of the soil samples was determined electrometrically on a 1:2.5 soil-water suspension, which was stirred constantly during the course of the measurement. All plant materials were dry-ashed at 500° C. and the various ash constituents determined by standard methods.

RESULTS AND DISCUSSION

Chemical analysis of acidified soil before planting

A chemical analysis of the acidified soil series which was made just before the first crop was planted appears in table 1. The soil treatments are designated by the pH values chosen for investigation. Though the measured pH values of the soils at the time of planting vary considerably from the values selected, the values achieved provide a fairly uniform distribution of acid reaction levels for soil and plant studies. Obviously, acidification of this soil results in an increase in water-soluble cations and a decrease in exchangeable cations. This effect is much more obvious for calcium and magnesium than for sodium and potassium, which are present in much smaller amounts. Although the sums of the exchangeable plus water-soluble ions for any one cation over the range of reactions studied are not identical, they appear sufficiently constant to suggest that the increase in water-soluble cations which occurs when this soil is acidified is due largely to replacement of these cations on the exchange complex by hydrogen.

Inasmuch as the acidified soils were not subjected to leaching between treatment and planting, the increase in conductivity which occurs with increasing acidity is to be expected. In light of subsequent discussion on the effect of acidification on crop yield, it should be noted that the conductivity of the most acid series (0.77 mmho/cm.) is decidedly on the low side of the range of salinity of 0–4 mmho/cm. which can be tolerated by all crops (8). Water-soluble phosphorus in this particular soil is increased by acidification, as is water-soluble manganese. Evidence has been obtained, however, in another study involving soil acidification (2) which shows that the solubility of phosphorus in some alkaline soils is decreased rather than increased by a lowering of the pH of the soil. This variability in phosphate solubility in soils which results from acidification is undoubtedly associated with the amount of calcium brought into solution simultaneously. Burd (3) has shown that the release of large quantities of calcium in proportion to phosphate depresses phosphate-ion solubility.

Yield and composition of alfalfa

The influence of acidification on the yield and composition of alfalfa plants is reported in table 2. In treatment series 1, which involves acidified soil without added phosphorus, yield falls off perceptibly at pH 4.0 and is exceedingly small at pH 3.0. Although the percentage germination and time of emergence appeared not to be affected over the range of reactions studied, impaired growth of plants in soil at pH 4.0 and 3.0 was noted. These plants were small and spindly on emergence and were definitely retarded at subsequent stages of growth. The addition of treble superphosphate to the soils in treatment series 2 does not appear to have influenced the effect of increasing acidity on the yield of alfalfa. Yields at pH 4.0 and 3.0 are similar to those in treatment 1.

The yield of alfalfa in pots irrigated with acidified water (treatment series 3) does not vary appreciably from treatment to treatment. Apparently the amount of acid added to the soil in the irrigation water was not sufficient to impair growth.

The information in tables 1 and 2 strongly suggests that the reduced yield of alfalfa is associated with acidity and not with insufficient calcium, for the sum of the exchangeable and water-soluble calcium in the soil is approximately constant over the entire range of reactions studied.

The data on plant composition in table 2 indicate that acidification has appreciably increased the percentage of K, Mg, Na, P, and S in plants grown in the pH 4.0 and 3.0 soil treatments. These results are in agreement with information published by Albrecht and Schroeder (1) who found a greater uptake of nutrients by plants in acid soils than in neutral soils. The phosphorus content of plants grown in treatment series 2, which received phosphorus at the rate of 200 pounds P_2O_5 per acre, is generally higher than that of plants grown in treatment series 1, to which no phosphate was added. The increased phosphorus intake by plants in series 2 is accompanied by a reduced sulfur intake, if the sulfur levels of plants grown in series 1 are used as a basis of comparison.

TABLE 2

Yield and composition of leaves and stems of alfalfa grown in acidified Ramona sandy loam

TREATMENT	YIELD*	Ca*	Mg	Na	K	P	S
	gm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Series 1							
pH 7.0 soil	11.6	1.35	.259	.235	1.94	.207	.272
pH 6.0 soil	10.2	1.41	.237	.233	2.19	.183	.260
pH 5.0 soil	11.1	1.37	.248	.217	2.07	.232	.261
pH 4.0 soil	8.5	1.46	.324	.293	2.11	.308	.362
pH 3.0 soil	2.3	1.33	.341	.347	3.12	.325	.549
Series 2							
pH 7.0 soil + P_2O_5†	13.4	1.45	.264	.135	1.63	.231	.225
pH 6.0 soil + P_2O_5	11.6	1.40	.253	.172	1.78	.286	.230
pH 5.0 soil + P_2O_5	11.7	1.35	.256	.120	1.86	.273	.233
pH 4.0 soil + P_2O_5	10.6	1.43	.309	.200	2.03	.345	.297
pH 3.0 soil + P_2O_5	3.3	1.48	.409	.385	3.00	.389	.414
Series 3							
pH 6.0 H_2O	9.1	1.42	.260	.243	2.13	.258	.294
pH 5.0 H_2O	9.9	1.48	.285	.232	1.83	.226	.306
pH 4.0 H_2O	9.8	1.40	.269	.248	1.97	.215	.294
pH 3.0 H_2O	8.9	1.49	.281	.231	2.00	.244	.327

* Average of three replicates.

† Applied as treble superphosphate at the rate of 200 pounds P_2O_5 per acre.

Yield and composition of sweet orange seedlings

The yield and composition of 1-year-old sweet orange seedlings which were grown for 8 months in the same soil used for growing the alfalfa are shown in table 3. Contrary to the trend found for alfalfa, growth of citrus seedlings in treatment series 1 and 2 is definitely improved at the more acid pH levels. These plants were not only taller but had larger stems and leaves than the plants grown at the higher pH levels. During the first 5 months of growth, seedlings in series 2 appeared to be more vigorous than seedlings grown at comparable pH levels in series 1. This suggested that a phosphorus response was being obtained on this soil. In the seventh and eighth months of growth, however, the differences in vigor between plants in the two series grown at the more acid level became less apparent. The yields of plants grown in pots irrigated with acidified water indicate that growth was improved at pH 5.0, 4.0, and 3.0. Though they show that greatest growth in this series took place at the pH 5.0 level, the differences at pH 5.0, 4.0, and 3.0 are probably not significant.

TABLE 3

Yield and composition of sweet orange seedlings grown in acidified Romana sandy loam

TREATMENT	YIELD*	Ca†	Mg	K	P	S	Mn
	gm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*ppm.*
Series 1							
pH 7.0 soil	34.3	3.49	.216	1.77	.122	.214	14
pH 6.0 soil	32.0	3.76	.250	1.87	.130	.234	15
pH 5.0 soil	35.9	3.82	.219	1.67	.122	.221	16
pH 4.0 soil	41.0	3.67	.206	1.67	.126	.219	17
pH 3.0 soil	40.6	3.56	.220	1.71	.134	.238	49
Series 2							
pH 7.0 soil + P_2O_5‡	36.8	4.04	.268	1.78	.124	.207	16
pH 6.0 soil + P_2O_5	38.4	4.10	.260	1.92	.142	.206	15
pH 5.0 soil + P_2O_5	38.0	4.06	.213	1.57	.149	.231	18
pH 4.0 soil + P_2O_5	40.1	4.09	.225	1.43	.151	.248	20
pH 3.0 soil + P_2O_5	43.6	4.13	.215	1.41	.166	.234	42
Series 3							
pH 6.0 H_2O	31.1	3.55	.240	2.00	.123	.234	18
pH 5.0 H_2O	38.3	3.91	.258	2.03	.121	.280	20
pH 4.0 H_2O	37.5	4.06	.274	2.19	.140	.285	15
pH 3.0 H_2O	35.9	3.82	.245	2.09	.126	.311	17

* Average of three replicates. This figure includes the weights of stem and leaves.

† The plant analyses were made on leaves.

‡ Applied as treble superphosphate at the rate of 200 pounds P_2O_5 per acre.

The influence of various levels of acidity on the composition of sweet orange seedling leaves is by no means so consistent as it is on alfalfa leaves. In series 1, the amounts of various constituents found at the various pH levels are relatively uniform. In series 2, phosphorus definitely increases with decreasing acidity as does sulfur. Magnesium and potassium, however, decrease with decreasing pH, and calcium remains fairly constant although definitely higher than in treatment 1. These findings suggest a reciprocal relationship between phosphorus and potassium or magnesium. Though this relationship for magnesium and phosphorus has not been noted elsewhere, similar data involving potassium and phosphorus in citrus leaves are soon to be published[2] in connection with studies involving a long-term fertilizer trial. Additional information must be obtained before any general conclusions can be drawn regarding a possible interrelationship between potassium and phosphorus.

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[2] By W. W. Jones of this station.

The total manganese content of the leaves increases gradually at pH 4.0 and rises sharply at pH 3.0 in series 1 and 2. These results are in accord with the idea that the availability of compounds like iron, zinc, and manganese is increased by acidification.

The application of acidified irrigation water has increased the sulfur content of the leaves but otherwise seems to have had little effect on plant composition.

TABLE 4

Effect of 1 year of irrigation and cropping on the pH and water-soluble Mn and P in acidified Ramona sandy loam

TREATMENT	pH OF 1:2.5 SOIL-WATER SUSPENSION	H_2O-SOLUBLE Mn	H_2O-SOLUBLE P
		ppm.	*ppm.*
Series 1			
pH 7.0 soil*	7.6	0	0.33
pH 6.0 soil	7.7	0	0.58
pH 5.0 soil	7.7	0	0.80
pH 4.0 soil	7.6	0	1.17
pH 3.0 soil	6.7	0	5.00
Series 2			
pH 7.0 soil + P_2O_5†	7.7	0	1.80
pH 6.0 soil + P_2O_5	7.7	0	2.66
pH 5.0 soil + P_2O_5	7.6	0	3.80
pH 4.0 soil + P_2O_5	7.5	0	6.90
pH 3.0 soil + P_2O_5	6.7	0	12.90
Series 3			
pH 6.0 H_2O	7.1	0	0.25
pH 5.0 H_2O	6.5	0	0.29
pH 4.0 H_2O	6.2	0	0.63
pH 3.0 H_2O	5.3	1.0	1.93

* Untreated soil.

† Applied as treble superphosphate at the rate of 200 pounds P_2O_5 per acre.

Although it is quite evident that acidification has increased the growth of citrus seedlings in this soil, table 3 reveals that such growth increases cannot be correlated with the increased uptake of ions reported in this study. Since all ions in table 3 appear to be present in adequate amounts at all levels of acidity, the differences in growth must be attributed to the influence of pH on other factors or on the availability of other ions not investigated.

Chemical analysis of soil after cropping

To obtain some idea of the influence of cropping and irrigation on soil reaction and nutrient availability, a number of chemical measurements were made on the soil from each treatment immediately following removal of the citrus seedlings. The results are recorded in table 4. The only soils in series 1 and 2 which are acid after being irrigated for 1 year with water of pH 8.0 are those which were acidified initially to pH 3.0. On the other hand, soils of series 3, which were not acidified initially, have been made progressively more acid through irrigation with water acidified to different levels. The relationship between these changes in reaction and the solubility of phosphorus and manganese at the start and conclusion of the experiment is of considerable interest. The solubility of phosphorus in series 1 at the end of the experiment is very similar to that at the beginning despite the fact that the pH of the first four levels of reaction are above 7.5 at the end of the experiment. This same relationship exists in series 2, although the amount of phosphorus soluble at the end of the experiment has been greatly increased at each reaction level by the addition of treble superphosphate to the soil at planting time. The large quantities of water-soluble phosphorus present at the various reaction levels in treatment series 2 undoubtedly account for the increased uptake of this nutrient by the sweet orange seedlings of this series.

The solubility of manganese in the soil at the end of this experiment, on the other hand, is not correlated with the initial pH but with the final pH, for a measurable amount of water-soluble manganese is found only in soil receiving the most acid irrigation water.

In view of the fact that the manganese content of the plants is exceedingly well correlated with the quantities of manganese released initially by direct soil acidification, the lack of soluble manganese in the soils at the conclusion of cropping may be attributed in large measure to withdrawal by the plants. Otherwise, one would have to assume that the reactions involved in reverting soluble manganese to insoluble forms under alkaline conditions proceed with greater efficacy than those involved in phosphate reversion. Further work on the chemistry of soil manganese in relation to soil acidification is now in progress in this laboratory.

CONCLUSIONS

The data pertaining to soils and plants are illustrative of the information that has been obtained in soil acidification studies in this laboratory.

So far as the soil is concerned, the existing experimental data indicate that the following reactions occur when acid amendments are applied to alkaline soils: (*a*) exchangeable cations are replaced by hydrogen, thereby increasing the amount of water-soluble cations; (*b*) depending upon the amount of calcium that is released, the solubility of soil phosphates may be increased or decreased; (*c*) the solubility of metallic ions such as copper, manganese, iron, and zinc is increased.

Although the concentration of a number of essential plant nutrients is increased by acidification, the significance of this increase with respect to plant growth cannot be fully established at this time. The experiments reported show that some plants respond favorably to acidification whereas others respond unfavorably. A vast amount of additional data derived from greenhouse and field studies must be obtained before soil acidification can be recommended as an approved cultural practice for alkaline soils.

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SOIL SCIENCE

VOLUME 70 *August 1950* NUMBER 2

MINOR-ELEMENT CONTENT OF LEAVES FROM TUNG ORCHARDS

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Received for publication December 27, 1949

Minor-element nutrition is one of the most important considerations in growing tung trees commercially in the southeastern United States. Most of the soils in the tung-producing areas are comparatively low in one or more of the minor elements zinc, copper, manganese, boron and iron. This is especially true of the lighter textured soils that predominate in peninsular Florida. The pH of the soils in most tung orchards down to 12 inches ranges from 5.0 to 5.8.

Leaf analysis has been most helpful in the diagnosis and correction of minor-element deficiencies of tung. Many data on minor-element content of leaves have been obtained during the last 7 years in connection with various field experiments on a wide variety of soils. From these data, some representative zinc, copper, manganese, boron and iron analyses have been selected for presentation here. These are discussed in relation to the kind of soil on which the trees are growing, the kind and amount of fertilizer applied, and the incidence and severity of leaf symptoms.

METHODS

The same principles were used in collecting leaf samples from tung trees as have been established with other tree crops. Leaf blades without the petioles were taken from the middles of the shoots of modal length usually in August when shoot growth was completed for the year; the fruits were of full size, and oil formation was rapidly underway. The sample usually consisted of about 100 leaves composited from not less than six trees that constituted an experimental plot or a representative area in an orchard. In general orchard sampling, each distinct area, as indicated by a difference in type of soil or growth conditions of the trees, was sampled separately. Two or more replicates of composite samples were taken from each area or experimental treatment. Leaves with necrotic tissue were avoided.

It was not found necessary to wash the leaves before drying. During the summer rainy season contamination with dust is negligible, and commercial tung orchards ordinarily are not sprayed.

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[1] Acknowledgment is due the following members and former members of the U. S. Field Laboratories for Tung Investigations who furnished many of the leaf samples: Joseph Hamilton, the late George M. Bahrt, Ralph T. Brown, Marshall S. Neff, John H. Painter, and Benjamin G. Sitton.

As soon as possible after sampling, the leaves were dried in an oven at 70° C. with forced ventilation. After drying they were ground in a standard intermediate Wiley mill, which is equipped with stainless steel knives and sieves. It was found that contamination from this mill was negligible.

The samples were dry-ashed in a muffle furnace in platinum dishes at a temperature of about 480° C. for about 6 hours. Under these conditions and in the presence of tung leaf tissue, loss by volatilization, even of boron, is negligible. Depending on the quantity of the minor elements present in the samples, 2 to 10 gm. of material were ashed. The ash was taken up in the minimum amount of HCl necessary for complete solution after digestion on a hot plate for about 1 hour. For a 2-gm. sample, about 15 ml. of *N* HCl was adequate. The solution was filtered only if necessary and was made up to volume in a 100-ml. volumetric flask.

In dissolving the ash and in subsequent operations, the usual precautions were taken to provide minor-element-free solutions and glassware. Sufficiently pure water was obtained simply by passing distilled water through a column of Amberlite IR-100. Chemicals were tested and purified if necessary.

Zinc was determined essentially as outlined by Cowling and Miller (1), copper by the carbamate method (3), manganese by the standard perodate method, boron by the turmeric method (5), and iron by the *o*-phenanthroline method (4).

The results were calculated on the basis of parts per million of dry matter.

RESULTS OF ANALYSES AND DISCUSSION

Zinc

The zinc content of tung leaves from trees on various soil types receiving different treatments is given in table 1. It will be noted that the zinc content of the leaves ranges from 10 ppm. to 229. Leaves from trees on both the coarse and fine textured soils in Florida have a very low zinc content, 10 to 15 ppm., where no zinc sulfate has been applied. Usually these leaves show severe deficiency symptoms. A 2- to 4-ounce soil application of zinc sulfate per tree per year ordinarily corrects the deficiency and increases the zinc content to 30 or more parts per million. Occasionally on some soils this application of zinc sulfate fails to control the deficiency, especially with rapidly growing 1- and 2-year-old trees.

Tung trees in Alabama, Mississippi, and Louisiana show less zinc deficiency than those in Florida, even on the same or closely related soil types. Nevertheless, many orchards in these states show the deficiency, especially in the early years, and these require zinc fertilizers. The accumulation of 229 ppm. zinc in the leaves of the trees at Fairhope, Alabama, after a soil application of zinc sulfate is striking. Although this is the highest amount of zinc found in leaves under commercial orchard conditions, there was no evidence of any toxicity.

Table 2 gives more details on the zinc content of tung leaves in relation to the degree of deficiency symptoms. Although the trees received a soil application of 2 ounces of zinc sulfate per tree per year, many of them showed zinc-deficiency symptoms in varying degree. It appears that slight symptoms show up when the zinc content drops to about 26 ppm. The zinc content decreases with in-

TABLE 1

Zinc content of tung leaves from trees on different soils receiving various treatments

Dry-matter basis

LOCATION	AGE OF TREES	SOIL TYPE	ZINC SULFATE APPLIED PER TREE*	LEAF-DEFICIENCY SYMPTOMS	ZINC
	yr.				*ppm.*
Gainesville, Fla.	1	Arredondo fine sandy loam	None	Severe	15
Gainesville, Fla.	1	Arredondo fine sandy loam	4 oz.	None	30
Alachua, Fla.	1	Gainesville fine sandy loam	None	Severe	14
LaCrosse, Fla.	2	Lakeland fine sand	2 oz./yr.	None	73
Reddick, Fla.	7	Arredondo loamy fine sand	None	Severe	11
Lloyd, Fla.	6	Red Bay fine sandy loam	None	Severe	10
Capps, Fla.	6	Red Bay fine sandy loam	2 oz./yr.	None	36
Milton, Fla.	12	Orangeburg loamy sand	None	Moderate	14
Milton, Fla.	12	Orangeburg loamy sand	1 lb./yr. last 2 years	None	67
Lamont, Fla.	2	Faceville fine sandy loam	4 oz./yr.	Moderate	15
Monticello, Fla.	10	Ruston fine sandy loam	2 oz./yr.	None	42
Irvington, Ala.	12	Tifton fine sandy loam	None	Slight	19
Fairhope, Ala.	6	Norfolk fine sandy loam	None	None	33
Fairhope, Ala.	6	Norfolk fine sandy loam	1 lb.†	None	229
Petal, Miss.	2	Norfolk fine sandy loam	None	Slight	24
Lumberton, Miss.	5	Ruston loamy fine sand	None	Slight	29
Bush, La.	12	Savannah very fine sandy loam	None	None	29
Folsom, La.	7	Ora very fine sandy loam	None	None	38
Folsom, La.	5	Savannah very fine sandy loam	None	Slight	21

* Soil application of dry salt under spread of branches.

† 100 pounds per acre broadcast previous 5 years.

TABLE 2

Zinc content of tung leaves showing different degrees of leaf-deficiency symptoms

Dry-matter basis

LOCATION	AGE OF TREES	SOIL TYPE	LEAF-DEFICIENCY SYMPTOMS*	ZINC†
	yr.			*ppm.*
Gainesville, Fla.	2	Arredondo loamy fine sand	0	36
			1	22
			2	16
			3	12
			4	12
Hague, Fla.	1	Gainesville fine sandy loam	0	35
			1	26
			2	26
			3	18
			4	10

* On scale from 0 equals no deficiency symptoms to 4 equals very severe symptoms. Trees received a soil application of 2 ounces of zinc sulfate per tree per year.

† Mean of duplicate composite samples.

creasing severity of the symptoms. Leaves from trees showing the most severe symptoms have only 10 to 12 ppm. zinc.

Copper

The copper content of tung leaves from trees on different soils receiving various copper treatments is given in table 3. The copper content ranges from 2.5 ppm. to 12.4 ppm., which is representative for most leaf samples collected in August in commercial tung orchards. This is a relatively narrow range in comparison with that of the other minor elements.

TABLE 3

Copper content of tung leaves from trees on different soils receiving various treatments

Dry-matter basis

LOCATION	AGE OF TREES	SOIL TYPE	COPPER SULFATE APPLIED PER TREE*	LEAF-DEFICIENCY SYMPTOMS	COPPER
	yr.				*ppm.*
Alachua, Fla.	1	Gainesville fine sandy loam	None	Severe	2.9
Alachua, Fla.	1	Gainesville fine sandy loam	⅛ oz. in solution	None	4.0
Alachua, Fla.	2	Fort Meade loamy fine sand	None	Severe	2.8
Alachua, Fla.	2	Fort Meade loamy fine sand	4 oz. 2nd year	None	4.5
Alachua, Fla.	2	Arredondo loamy fine sand	½ oz./yr.	Severe	2.3
Alachua, Fla.	2	Arredondo loamy fine sand	3 oz./yr.	Slight	3.4
Morriston, Fla.	10	Fort Meade loamy fine sand	None	Severe	2.5
Morriston, Fla.	10	Arredondo loamy fine sand	None	None	5.2
LaCrosse, Fla.	2	Lakeland fine sand	None	None	4.9
Inverness, Fla.	8	Lakeland fine sand	1 oz./yr.	None	5.2
Brooker, Fla.	4	Arredondo loamy fine sand	2 oz./yr.	None	7.7
LaCrosse, Fla.	10	Leon fine sand	None	None	6.2
Lamont, Fla.	10	Ruston fine sandy loam	None	None	8.3
Monticello, Fla.	10	Faceville fine sandy loam	None	None	9.5
Cairo, Ga.	5	Red Bay fine sandy loam	None	None	6.4
Fairhope, Ala.	6	Norfolk fine sandy loam	None	None	12.0
Fairhope, Ala.	6	Norfolk fine sandy loam	¾ lb.†	None	12.4
Carriere, Miss.	1	Ora very fine sandy loam	None	None	6.4
Folsom, La.	12	Savannah very fine sandy loam	None	None	10.8
Bush, La.	10	Ora very fine sandy loam	None	None	11.4

* As the dry salt under the spread of the branches unless otherwise indicated.

† 40 pounds per acre broadcast previous 5 years.

It appears that leaves having less than about 3.5 ppm. copper show deficiency symptoms. No symptoms are apparent on leaves having more than 4 ppm. copper.

Soils of the Arredondo, Fort Meade, and Gainesville series in peninsular Florida apparently cannot often supply enough copper to maintain normal growth of tung trees, as shown by the severe leaf-deficiency symptoms of untreated trees. A small amount of copper sulfate usually corrects the deficiency on these soils, but not always. In several experiments as much as 3 ounces per tree per year failed to correct entirely the leaf symptoms in 2- and 3-year-old trees. Further details on the control of copper deficiency have been published elsewhere (2).

It is to be noted that leaves from trees on the finer textured soils of northern Florida, southern Georgia, Alabama, Mississippi, and Louisiana are relatively high in copper. No copper-deficiency symptoms of tung have been observed or reported on these soils. Copper sulfate applied to these soils has not increased the copper content of the leaves appreciably, as illustrated by the results in table 3 from the Fairhope, Alabama, orchard.

TABLE 4

Manganese content of tung leaves from trees on different soils receiving various treatments

Dry-matter basis

LOCATION	AGE OF TREES	SOIL TYPE	MANGANESE SULFATE APPLIED PER TREE*	LEAF-DEFICIENCY SYMPTOMS	MANGANESE
	yr.				*ppm.*
Gainesville, Fla.	18	Arredondo loamy fine sand	None	Moderate	30
Gainesville, Fla.	18	Arredondo loamy fine sand	1 lb. last 2 years	None	80
Reddick, Fla.	10	Arredondo loamy fine sand	None	Severe	25
Reddick, Fla.	10	Arredondo loamy fine sand	2 lb. last 2 years	None	100
Reddick, Fla.	10	Arredondo loamy fine sand	4 lb. last 2 years	None	322
LaCrosse, Fla.	10	Leon fine sand	None	None	90
Morriston, Fla.	8	Lakeland fine sand	None	Slight	36
Alachua, Fla.	2	Gainesville loamy fine sand	None	Slight	38
Alachua, Fla.	2	Gainesville loamy fine sand	4 oz./yr.	None	1,117
Alachua, Fla.	1	Gainesville loamy fine sand	2 oz.	None	113
Ocala, Fla.	1	Lakeland fine sand	2 oz.	None	402
Lamont, Fla.	10	Ruston fine sandy loam	None	None	1,846
Capps, Fla.	8	Red Bay fine sandy loam	None	None	2,884
Monticello, Fla.	10	Faceville fine sandy loam	None	None	572
Cairo, Ga.	5	Red Bay fine sandy loam	None	None	588
Fairhope, Ala.	6	Norfolk fine sandy loam	None	None	1,610
Fairhope, Ala.	6	Norfolk fine sandy loam	1 lb.†	None	1,812
Poplarville, Miss.	5	Norfolk fine sandy loam	None	None	902
Magnolia, Miss.	10	Ruston fine sandy loam	None	None	249
Folsom, La.	3	Savannah very fine sandy loam	None	None	637
Bush, La.	8	Ora very fine sandy loam	None	None	836

* Applied as the dry salt under the spread of the branches.

† 240 pounds per acre broadcast previous 5 years.

Manganese

The manganese content of tung leaves from trees on different soils receiving various treatments is given in table 4. The striking feature of these results is the wide range in the manganese content of the leaves, depending on the soil type and treatment. The leaves from deficient trees have less than 40 ppm. manganese, and those from normal-appearing trees have up to almost 2,900 pp. This range is representative of all the August midshoot-leaf samples from commercial tung orchards that have been analyzed.

As with copper and zinc, the manganese is lowest in leaves from trees on the sandy soils of peninsular Florida. Manganese-deficiency symptoms are common in that area but are easily corrected by soil applications of manganese sulfate.

The fine textured soils of northern Florida, southern Georgia, and the tung-growing sections of Alabama, Mississippi, and Louisiana appear to supply more than enough manganese to meet the needs of tung trees, as evidenced by the high manganese content of their leaves and the absence of deficiency symptoms. Although the leaves from these soils are comparatively high in manganese, there is a wide variation in content even on the same soil type in the same field. For example, in one experiment near Fairhope, Alabama, on Norfolk fine sandy loam, trees from two plots receiving the same treatment, which did not include manganese, had essentially the same leaf content of nitrogen, phosphorus, potassium, calcium, magnesium, zinc, and copper, but the manganese content in one plot averaged about 1,000 ppm. and in the other about 2,000 ppm.

Apparently tung trees can accumulate large amounts of manganese without causing iron deficiency. This indicates that the iron-manganese ratio in tung leaves under field conditions has no special significance. This matter has been explored in this laboratory and will be the subject of a later report.

It is interesting to note that, as in the case of copper, a soil application of manganese sulfate to Norfolk fine sandy loam at Fairhope, Alabama, has not increased the manganese content of the leaves appreciably.

Boron

The boron content of tung leaves from trees on different soils receiving different treatments is given in table 5. As boron deficiency in commercial tung orchards has not yet been observed and soil applications of boron have not yet been conclusively shown to be beneficial, only a limited number of leaf samples have been analyzed for boron. Apparently the type of soil does not have a great effect on the boron content of tung leaves, as the boron content of leaves from trees on the sandy soils of pensinsular Florida differ little from that of leaves on the finer textured soils. The range of leaf-boron content of trees on untreated soils is 38 to 75 ppm. which is relatively narrow.

As with many other crops, tung trees are sensitive to small soil applications of boron. A 4-ounce application of borax to 3-year-old tung trees on Lakeland fine sand caused severe burning of the foliage and increased the boron content to 226 ppm. Even on the finer textured soils, a 2½-ounce application of boron per year over a 7-year period increased the boron content to 158 ppm. and caused some toxicity symptoms.

TABLE 5

Boron content of tung leaves from trees on different soils receiving various treatments

Dry-matter basis

LOCATION	AGE OF TREES	SOIL TYPE	BORAX APPLIED PER TREE*	LEAF SYMPTOMS	BORON
	yr.				*ppm.*
Gainesville, Fla.	3	Lakeland fine sand	None	None	65
Gainesvile, Fla.	3	Lakeland fine sand	4 oz. 3rd year	Severe toxicity	226
LaCrosse, Fla.	2	Arredondo loamy fine sand	None	None	38
Alachua, Fla.	5	Gainesville fine sandy loam	None	None	56
Morriston, Fla.	15	Arredondo loamy fine sand	None	None	51
Morriston, Fla.	15	Arredondo loamy fine sand	5 oz. last year	Moderate toxicity	191
Capps, Fla.	4	Red Bay fine sandy loam	None	None	47
Lloyd, Fla.	6	Faceville fine sandy loam	None	None	62
Poplarville, Miss.	5	Savannah fine sandy loam	None	None	71
Poplarville, Miss.	5	Savannah fine sandy loam	3 oz. last 3 years	Slight toxicity	231
Lucedale, Miss.	13	Red Bay fine sandy loam	None	None	75
Lucedale, Miss	13	Red Bay fine sandy loam	2½oz. last 7 years	Slight toxicity	158

* Applied as the dry salt under the spread of the branches.

TABLE 6

Iron content of tung leaves from trees on different soils

Dry-matter basis

LOCATION	AGE OF TREES	SOIL TYPE	LEAF-DEFICIENCY SYMPTOMS	IRON
	yr.			*ppm.*
Gainesville, Fla.	15	Arredondo fine sandy loam	None	60
Gainesville, Fla.	1	Lakeland fine sand	None	69
Alachua, Fla.	1	Gainesville fine sandy loam	None	53
Ocala, Fla.	1	Lakeland fine sand	None	51
LaCrosse, Fla.	10	Leon fine sand	None	60
LaCrosse, Fla.	10	Leon fine sand	Moderate	35
Reddick, Fla.	10	Arredondo loamy fine sand	None	80
Lamont, Fla.	8	Ruston fine sandy loam	None	92
Monticello, Fla.	10	Red Bay fine sandy loam	None	60
Irvington, Ala.	10	Tifton fine sandy loam	None	86
Lucedale, Miss.	10	Red Bay fine sandy loam	None	72
Folsom, La.	6	Savannah very fine sandy loam	None	67
Bush, La.	8	Ora very fine sandy loam	None	75

Iron

The iron content of tung leaves on different soil types is given in table 6. It is surprising to note the relatively narrow range, 35 to 92 ppm., of iron in tung leaves despite the widely different soil conditions. Trees on the sandy soils, some of which contain only a small amount of total iron, have just about as much iron in the leaves as those on the fine textured soils, which have a relatively large amount of total iron, especially in the subsoil. Also the acidity of the latter is usually greater than that of the sandy soils in peninsular Florida.

Iron deficiency has been observed on only a relatively few trees in a limited area in Florida, and only one sample of leaves from deficient trees was available for analysis. This sample contained 35 ppm. iron in comparison with leaves from adjacent normal trees which contained 60 ppm.

SUMMARY

The zinc, copper, manganese, boron, and iron contents of representative tung-leaf samples are discussed in relation to the kind of soil on which the trees are growing and the kind and amount of fertilizer applied. Under all conditions observed, the range in zinc content of tung leaves was found to be 10 to 229 ppm., copper 2.5 to 12.4, manganese 25 to 2,884, boron 38 to 226, and iron 35 to 92.

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BORON IN OREGON SOILS AND PLANT NUTRITION[1]

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Received for publication September 26, 1949

In earlier reports the value of supplying boron to different Oregon soils for improving the yield and quality of alfalfa (3, 5), beets (6), and celery (2) and to prevent broccoli discoloration (8) and walnut snakehead (9) was established. Boron deficiency in Oregon has been identified with the lighter textured soils, acid peats, or older leached soils in the more humid area and with a few coarse textured, nearly neutral soils that have been heavily irrigated for a generation with nearly pure water (4). Toxic accumulations of boron occur locally in poorly drained, alkaline soil areas of Eastern Oregon. A preliminary map based on several hundred boron determinations showing the boron status and needs of Oregon soils has already been published (4).

During the past decade, attention has been given to determination of boron-deficient soil types or areas, optimum and critical concentrations of boron for various soils and crops, and effect of boron on plant-tissue composition. Boron-sensitive plants, especially on weakly buffered soils, appear to have a very narrow range of tolerance. The purpose here is to report information on optimum and critical concentrations of available boron in Oregon soils in relation to plant nutrition.

EXPERIMENTAL

Boron trials have been included in two blocks of randomized Latin square type field plot tests on Chehalis silty clay loam, with eight replications, during the past decade. Numerous other replicated field plots and greenhouse trials were made with different applications of boron. A garden has been maintained for several years to determine the effects of boron applications in light to heavy amounts on several kinds of vegetable and field crops.

Leaching experiments were conducted on Melbourne silt loam and Klamath peat that carried toxic concentrations of available boron. Various treatments were tested to learn their relative values in overcoming toxicity.

Determinations of boron in soils and plant parts were made by the method of Berger and Truog (1).

Rates of use of boron on alfalfa

In a boron-variation trial with an old stand of alfalfa on Willamette silty clay loam, treated in June 1936, there were applications of 0, 10, 20, and 30 pounds an acre of boric acid and four comparisons: light, medium, and heavy irrigation versus no irrigation. Yields increased with adequate irrigation and with increase in rate of boron. With the heaviest boron application, the cutting taken in dry weather increased threefold. The 20-pound rate of application resulted in an increase of 2.1 tons per acre of hay in 1938. The plant contents of boron, protein, and chlorophyll were increased by the boric acid application (5). Needed boron has promoted blooming and branching and increased resistance to drought and to competition by grass. The boron treatment, where needed, has favored longevity of alfalfa.

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[1] Published as Technical Paper 585 of the Oregon Agricultural Experiment Station, department of soils, drainage, and irrigation.

When boric acid was applied to Amity silty clay loam at 10, 20, and 30 pounds an acre, the heaviest application increased the alfalfa hay yield 1.26 tons per acre, an obviously significant and profitable increase.

In greenhouse trials, borax was applied to Camas gravelly loam at rates of 0, 10, 20, 40, 80, and 100 pounds, with four replications. The 20-pound rate resulted in definitely higher yields even to the fifth cutting in this poorly buffered sandy soil. The boron content of parts of alfalfa above ground increased from 10 ppm. untreated to 30 ppm. with 80-pound borax application. This soil was limed, and Bountiful beans were used as an indicator crop. The 10-pound application of borax resulted in more growth than did heavier applications.

In a Latin square type of experiment with eight replications, using plots 25 by 25 feet, the 5-year average gain in alfalfa hay yield was only 0.1 ton per acre from an application of 20 pounds borax every 2 years. The increase in 1945 was 0.77 ton. Statistical analysis indicates a 0.45-ton gain as significant. The gain comes in dry-weather cuttings when the borax treatment increases the leafiness and chlorophyll content by overcoming yellow-top. Borax produced no increase in 1949; possibly it is now present in excess.

In the second Latin square quad on Chehalis soil, borax applied as above gave a 3-year average increase in mint hay of 0.44 ton an acre, which is scarcely significant.[2] The mint oil yield or quality was only slightly improved in this test. On Clatskanie peat, borax treatment has frequently resulted in a slight increase of less than 1 per cent in menthol content (7).

Optimum and critical concentrations on Chehalis soil

Several vegetable crops have been included in field plots for the study of rates and methods of applying fertilizer containing boron to Chehalis silty clay loam. As the yield of bush beans has been erratic because of toxicity at the higher rates of application, the data are not included here. The treatments and data for tomatoes and corn are given in table 1. The rate of application was doubled in the spring of 1945 when the plots were retreated to induce toxicity or determine critical concentration.

Although sweet corn is moderately sensitive to boron, the maximum yield of roasting ears was obtained in 1945 where 160 pounds of borax an acre was applied. Symptoms of toxicity were noted on the foliage with the heavier rates of application. This 160-pound application also gave the maximum yield of tomatoes. That rate of application caused the greatest increase in boron in the

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[2] Ray Pendleton kindly checked the statistical analysis of data for this report.

TABLE 1

Optimum and critical boron concentrations for vegetables

CROP	BORAX APPLICATION		AVAIL. BORON IN TOP 7 INCHES SOIL	BORON IN PLANT PARTS			YIELD PER SQUARE ROD	CANKER OR CRACKS
	Method	Rate per A		Stem	Leaf	Fruit		
		lb.	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*lb.*	*per cent*
*Chehalis silty clay loam, 1943–1945**								
Tomatoes	Broadcast	20†	0.40	30	80	10	57	—
		40†	0.50	35	80	10	55	—
		80†	0.80	35	200	15	68	—
		160†	1.15	35	500	15	98	—
	Drilled	40	0.85	30	100	10	74	—
		80	1.00	30	80	8	80	—
	Check	0	0.30	25	20	6	67	—
	Spray	20	0.40	25	40	10	52	—
Corn	Broadcast	40	0.40	8	8	8	38.7	—
		80	0.50	10	10	10	55.8	—
		160	0.80	10	25	10	96 0	—
		320	1.25	25	100	10	48.1	—
	Drilled	40	0.85	4	8	4	44 9	—
		80	1.20	4	15	5	37.2	—
	Check	0	0.30	3	8	4	29.4	—
	Spray	20	0.40	4	8	4	46.5	—
Willamette silty clay, 1947‡								
Tomatoes	Check	0		9	30	10	275	—
	Broadcast	80		9	80	17	281	—
		160		17	85	45	102	—
		320		9	85	40	174	—
Corn	Check	0		7	23	6	Few ears	—
	Broadcast	80		9	60	7	—	—
		160		20	65	6	—	—
		320		20	95	6	—	—
Sunflowers	Check	0		15	45	57§	65 Av.	—
	Broadcast	80		17	75	55	—	—
		160		13	110	63	—	—
		320		18	160	70	—	—
Bountiful beans	Check	0		22	20	32	30	—
	Broadcast	80		65	23	35	36	—
		160		75	23	25	24	—
		320		70	25	25	18	—
Carrots	Check	0			28	9¶	248	—
	Broadcast	80			45	28	300	—
	(Flooded)	160			55	45	176	—
		320			65	55	108	—
Table beets	Check	0			23	20	184	—
	Broadcast	80			40	23	232	—
		160			55	23	160	—
		320			60	23	132	—

TABLE 1—*Continued*

CROP	BORAX APPLICATION		AVAIL. BORON IN TOP 7 INCHES SOIL	BORON IN PLANT PARTS				YIELD PER SQUARE ROD	CANKER OR CRACKS
	Method	Rate per A.		Stem	Lead	Fruit	Root		
		lb.	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*lb.*	*per cent*
			Willamette silty clay loam, 1948						
Carrots	Check	0	2.0	—	28	—	18	66	12
	Broadcast	80	3.0	—	30	—	20	71	4
		160	5.0	—	40	—	30	70	2
		320	10.0	—		—	40	72	4
Beets	Check	0	2.0	—	27	—	50	60	30
	Broadcast	80	3.0	—	27	—	30	90	20
		160	5.0	—	27	—	30	144	1
		320	10.0	—	35	—	40	96	0
Sunflowers	Check	0	2.0	—	40	—	28	150	—
	Broadcase	80	3.0	—	56	—	55	200	—
		160	5.0	—	50	—	32	255	—
		320	10.0	—	60	—	54	270	—

* Boron determinations by J. V. Jordan.

† Boron rate doubled in spring, 1945.

‡ Determinations by R. Date.

§ Pistils.

¶ Roots.

tomato leaf, a moderate increase in the stem of corn and tomatoes, and a slight increase in the fruit or ears. Applications of 10 to 40 pounds an acre, with the lighter rate for sandy soils or boron-sensitive plants, should generally supply borax needs for vegetable plantings without toxicity symptoms. The high boron tolerance obtained with two silty clay loam soils studied (table 1) is related to their high base-exchange capacity and buffer values.

Optimum and critical boron concentrations for various crops on Willamette silty clay loam

Several plantings were included in the study of optimum and critical concentrations of boron on Willamette silty clay in 1947 and 1948. The data are summarized in table 1. Eighty pounds of borax broadcast at planting time resulted in a maximum yield of tomatoes, Bountiful beans, carrots, and table beets. As corn produced few ears and sunflower seeds were not mature at harvest time, comparative yields were not taken for those crops. The two heavier applications caused toxicity symptoms on the foliage of the corn but caused no visible injury on the sunflower leaves. Toxicity symptoms, or discoloration of edges, as well as interior spotting, occurred in the lower leaves of the tomatoes, beans and, corn. Canker was prevalent on the untreated beet plot. It was substantially reduced by the 80-pound applications and was absent with the heavier applications of borax.

In general, the boron content of the stem, leaf, and fruit increased as the rate of application of boron was increased. This appears to be most marked in the stem of the fruit or ears. Sunflower pistils were high in boron.

In September 1947, the available soil boron of the untreated plot, 0- to 7-inch depth, was 0.55 ppm.; with 80-pound application it was 0.70 ppm.; with 160-pound application it was 0.90 ppm.; and with 320-pound application it was 1.75 ppm. For the 0- to 14-inch depth, boron penetration increased with rate of treatment from 2 ppm. for the control to 3, 5, and 6 ppm. with increased rates of application.

From these tests it would appear that beans are very sensitive to boron, that corn is fairly sensitive, and that beets, carrots, sunflowers, tomatoes, and alfalfa are relatively tolerant. In this test, 80 pounds was a favorable rate of application for tomatoes, sunflowers, carrots, and table beets in Willamette silty clay. The boron content of the parts of plants giving maximum yields appears to indicate a suitable supply.

Removal of excess boron

Melbourne silty clay loam treated with heavy applications of borax at the Camp Adair area to kill poison oak caused injury to all vegetation. Available boron in this soil when collected was 200 ppm.

The soil was set up in a series of 6-inch flower pots with triplicated treatments and subjected to leaching in the greenhouse for 2 years. It was found that heavy applications of oak litter aided removal of excess boron. Lime, sulfur, gypsum, or manure treatments were less effective than oak litter. The lime reduced the available-boron concentration. Leaching without other treatment proved to be a slow, yet effective, method of removing excess boron from the soil. In the 2-year period between March 1945 and March 1947, the available boron was reduced from 200 to less than 5 ppm. During the early part of the experiment, sunflowers, alsike clover, and Bountiful bean seed germinated, but all the sprouts yellowed and withered. Some faint toxicity symptoms were still evident with the bean as an indicator plant where the soil showed 3 ppm. of available boron. The oak litter and leaching reduced the concentration to 1.1 ppm. in the 2-year period.

Klamath peat from the experimental area in the lower Klamath marsh had a pH of 9.0 and was found to contain an objectionable amount of available boron, or 20 ppm. Table 2 summarizes an experiment conducted with the peat in the greenhouse to determine the value of heavy leaching and chemical treatment for removing excessive boron from the soil. Ten series of 5-gallon jars were set up, four or more applications being used. The treatments applied are indicated in table 2, which gives the yield of oats and beans, the amount of leachate, soil reaction, and available boron found after each crop. After treatment, the jars were incubated for 6 weeks and then planted to Banner oats, followed by beans.

The average yield of oat hay per replicate was 24.5 gm. for the check plots and 50.1 gm. for the plots receiving sulfur and lime. The manure-sulfur combination was not so effective in raising the yield as were the manure and sulfur treatments individually. Yet the manure and sulfur treatments were most effective in reducing the over-all pH of the peat to 7.29 and 7.75 respectively. Leaching the checks reduced the soil pH to 8.30. The leaching process alone reduced the available boron. The most effective treatment was liming, which tended to tie up part of the boron in unavailable form, thereby reducing the available boron to 4.5 ppm. Manure proved effective in reducing the amount of available boron to 5.5 ppm. The manure-sulfur combination reduced the boron to 8 ppm.

TABLE 2

Boron removal from Klamath peat by soil treatment and leaching

TREATMENT PER ACRE	NOVEMBER 1945 TO MAY 1946				MAY TO JULY 1946			
	Average Oat Hay Yield	Leachate	Soil pH*	Available Soil Boron†	Average Bean Yield‡	Leachate	Soil pH	Available Soil Boron
	gm.	*liters*		*ppm.*	*gm.*	*liters*		*ppm*
Checks	24.5	5.5	8.30	13	30.3	2.3	8.30	10
30 tons manure§	38.0	5.7	7.29	5.5	35.1	2.0	7.27	3
30 tons manure§ 1 ton Sulfur	32.8	5.6	7.98	8	35.4	2.5	7.96	5
30 tons manure§ 1 ton Lime	39.1	5.5	8.33	8	29.1	2.0	8.30	6
1 ton Sulfur¶	44.3	5.5	7.75	15	39.4	2.0	7.50	9
2 tons Gypsum¶	37.2	—‖	8.20	11	39.7	2.2	8.17	6
2 tons Lime¶	50.1	5.5	8.15	4.5	44.9	2.3	8.13	2.5
180 lbs. Borax¶	22.9	5.6	8.30	16	26.9	2.2	8.20	12

* Average pH of each replicate.

† Determination on composite soil samples from each treatment.

‡ Green weight of seven bean plants.

§ Six replications.

¶ Four replications.

‖ Two leachate jars leaked.

The heaviest growth of beans, 44.9 gm., was obtained from the lime pot, followed closely by the 39.7-gm. growth, with the gypsum treatment and then by the 39.4-gm. growth with the sulfur treatment. The manure and sulfur treatments were still the most effective in reducing the soil pH. The available boron was further reduced to 2.5 ppm. with the liming treatment and to 3 ppm. with the manure treatment. Boron-toxicity symptoms were not evident in bean plants grown on the soil that had 2.5 ppm. available boron. Leaves of the plants in other jars containing higher amounts of available boron were brittle and had some markings at the edges of the lower leaves.

Effect of boron on plant composition

Menthol. A slight increase in menthol content of mint oil has been found due to application of borax (7).

TABLE 3

Relation of available soil boron and plant nutrition

Field study on Chehalis silty clay loam

SOIL TREATMENT BORAX	SOIL AVAILABLE BORON	BORON AND NITROGEN IN PLANT PARTS					
		Stems		Leaves		Fruit	
		Boron	Nitrogen	Boron	Nitrogen	Boron	Nitrogen
		Tomatoes					
lb./A.	*ppm.*	*ppm.*	*per cent*	*ppm.*	*per cent*	*ppm.*	*per cent*
40-broadcast	0.40	30	1.97	80	4.22	10	2.26
80-broadcast	0.50	35	2.02	80	4.26	10	2.30
160-broadcast	0.80	35	2.08	200	4.24	15	2.29
320-broadcast	1.15	35	2.11	500	4.26	15	2.26
40-drilled	0.85	35	1.81	100	4.04	10	2.21
80-drilled	1.00	30	1.99	80	4.08	8	2.58
20-spray	0.40	25	1.86	40	4.26	10	2.17
Check	0.30	25	1.97	20	4.20	6	2.21
		Sweet corn					
40-broadcast	0.40	8	0.80	8	2.50	8*	3.19
80-broadcast	0.50	10	0.86	10	2.55	10	3.39
160-broadcast	0.80	10	0.82	25	2.53	10	3.51
320-broadcast	1.15	25	0.87	100	2.59	10	3.72
40-drilled	0.85	4	0.85	8	3.73	4	3.19
80-drilled	1.00	4	0.90	15	2.65	5	3.24
20-spray	0.40	4	0.80	8	2.48	4	3.13
Check	0.30	3	0.78	8	1.91	4	3.05

* Kernels only.

TABLE 4

Relation of available soil boron to nitrogen and boron content of bean leaves

Greenhouse study

SOIL TREATMENT B AS BORIC ACID	CHEHALIS SILTY CLAY LOAM			CAMAS GRAVELLY LOAM		
	Available soil boron	Bean leaf		Available soil boron	Bean leaf	
		Boron	Nitrogen		Boron	Nitrogen
lb./A.	*ppm.*	*ppm.*	*per cent*	*ppm.*	*ppm.*	*per cent*
Checks	0.4	30	2.97	0.3	25	2.92
5	0.6	50	3.27			
10	0.7	60	3.64	0.5	40	2.94
20				0.9	130	3.19
40				1.2	220	4.24

Nitrogen. Determinations of nitrogen in tomatoes, sweet corn, and beans grown with and without borax treatment on three different soils, made in 1945, showed higher total nitrogen content in two out of three instances where boron was applied.

Analyses of plant parts of sweet corn and tomatoes grown in Chehalis silty clay loam in the borax variation trials in 1945 (Table 3) indicate higher nitrogen contents at the toxic level.

Analyses of plants grown under controlled conditions in the greenhouse (Table 4) reveal consistent increase in leaf nitrogen with increase in leaf boron.

Chlorophyll. When boron overcomes the chlorotic condition or yellow-top of alfalfa, the greener alfalfa has been found to contain more chlorophyll (5).

Potatoes. The yield of potatoes has been increased moderately in some cases and depressed slightly in others by boron. Smoothness and grade quality appear to be improved. Potatoes are very sensitive to borax, which may be more safely used if broadcast at a reduced rate of a few pounds an acre on sandy soils.

DISCUSSION

Chemically pure boric acid was applied in very dilute solution with a garden sprinkler in early controlled experiments, but use of granular borax is usually cheaper for field use. Granular borax may be applied by broadcasting evenly and at the rate of 30 pounds an acre very early in the growing season. The boron treatment has been found to carry over at least 2 years. Borax may be applied as clover seed is sown or with landplaster in a drill.

Corn, potatoes, and beans may be injured by more than 15 to 30 pounds borax an acre or by less if drilled on medium textured soils. Alfalfa, beets, carrots, tomatoes, and sunflowers are relatively tolerant. Application of 30 pounds borax an acre has controlled alfalfa yellow-top; 50 pounds frequently has made more hay. For medium textured western Oregon soils this latter amount is mixed with 125 pounds of gypsum an acre or 150 pounds of superphosphate for sowing on alfalfa. If alfalfa is to be replaced by a boron-sensitive crop the following year, 30 pounds an acre may be safer. Two pounds of boric acid contains approximately as much of the element boron as does 3 pounds of borax. Borax may now be obtained from most fertilizer dealers.

The slightly higher efficiency from drilling or spraying may be more than offset by the convenience of broadcast applications. For moderately sensitive crops, borax may best be broadcast a week or 10 days before the planting date.

Use of boron on Eastern Oregon soils, except in limited areas, is not beyond the experimental stage. In Eastern Oregon there is little evidence of any deficiency except possibly on neutral soils with rapid drainage. Springdale sandy loam, Yakima gravelly loam, and Deschutes sandy loam are rather low in available boron.

With continued cropping, boron may become increasingly needed on leached soils. Deficiency symptoms may come to be recognized on various crops. A condition similar to alfalfa yellow-top has been observed on clover and on vetch and corrected by use of boron, though their boron requirements are much lower than that of alfalfa. Response of grasses in alfalfa plots treated with borax has been observed. It may be in part indirect.

Generally a second borax treatment should be delayed 2 or 3 years or until deficiency symptoms or soil or leaf analyses indicate need for further boron.

An excess of boron is highly toxic. Care should be taken in use of the nutrient. As indicated herein, liming will reduce concentration of available boron, whereas use of sulfur and manure with copious irrigation will hasten elimination of an excess from permeable soil.

SUMMARY

A study of optimum and critical boron concentrations with different soils and crops shows that alfalfa, table beets, carrots, and sunflowers are very tolerant to boron, whereas beans and tomatoes are very sensitive. The application for the former crops on medium textured, nearly neutral soils may be 30 to 50 pounds of borax an acre, whereas for potatoes and beans it must be limited to 10. A desirable level of available boron for such soil is 0.5 to 1.0 ppm.

Alfalfa may show yellow-top when the boron content is below 12 ppm. Thrifty plants on good alfalfa soils contain 20 to 50 ppm. boron.

Soil with an excess of available boron may be improved by drainage with applications of sulfur and manure and copious irrigation. If this is not feasible, liming may be used to aid solubility and activity of boron present.

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IDENTIFICATION OF MINERALS IN SOIL CLAY BY X-RAY DIFFRACTION PATTERNS

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X-ray diffraction data concerning minerals that may occur in the clay separate (particles $<2\mu$) of soils are widespread in the literature. They are found in ceramic, mineralogic, and crystallographic papers and in communications and bulletins from several agricultural stations. Urbain (45) and Nagelschmidt (39) have published x-ray data of some of these materials. Hanawalt *et al.* (16) and the American Society for Testing Materials (1) have published extensive data on respectively, some 1,000 and some 3,000 inorganic and organic specimens, including minerals that may be found in the clay separate of soils.

When the several data on these minerals are compared, however, great differences are generally observed. The reasons are twofold.

First, material analyzed by the various workers is impure. This is because some clay minerals (for example, illite) occurring in nature only in dimensions of $<2\mu$, unlike common minerals that can be obtained in a pure form in larger sizes, are generally contaminated by small amounts of other clay minerals, predominantly quartz and micas.

Second, in most of the papers, the thickness of the specimen or the eccentricity in regard to the center of the camera has been neglected. Both give rise to divergences in the real distance of the diffracted beams on the photo caused by the specimen itself. At low glancing angles especially, in which case the most characteristic patterns for identification of soil clay minerals are found, the divergence caused by thickness of the specimen is the greatest (table 1).

Finally, x-ray diffraction data of minerals, such as diaspore, lepidocrocite (iron rust), sepiolite, talc, and pyrophyllite, which do not occur in the clay separate of soils, or such as halloysite (10 A.), nontronite, attapulgite, and cristobalite, which occur only in particular sediments or layers from certain localities, are tabulated together with soil clay minerals.

The purpose of this paper is to give exact x-ray data on minerals that may occur especially in the clay separate ($<2\mu$) of soils so that identification of an x-ray pattern of an unknown clay sample is facilitated.

MINERALS

For comparable data, photos were obtained from particles $<2\mu$ (free from organic matter) which were isolated from soils (sediments) of different localities

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[1] The author is indebted to P. M. de Wolff (Laboratory for Physics, Technical University of Delft) and to D. W. Smits (Laboratory for Inorganic Chemistry, University of Groningen) for their advice during the course of this study, and to P. Kruizinga (Laboratory for Geology and Mineralogy, Technical University of Delft) for samples of pure minerals.

by the Atterberg sedimentation method. This was done because patterns of mineral particles of this size are much broader and more diffuse than patterns from coarser particles.

Except in a few cases in which no purer soil clay mineral $<2\mu$ was available, grinding to obtain particles $<2\mu$ was omitted, as by this procedure the reflections are broadened as a result of disturbed faces.

Extensive x-ray data are also given for glycerol-treated halloysite (10 A.), montmorillonite, and nontronite, which are clay minerals with basal spacings varying enormously with the amount of water between the layers. The glycerol method for clay minerals as proposed by MacEwan (30) was followed, because with this procedure constant basal data of high intensity can be obtained. Thus, especially if montmorillonite is only a minor component in soil clays, diffraction effects from this mineral are more easily discerned than those of the untreated sample. Further, for completeness, x-ray data are also given of certain minerals occurring only in the clay ($<2\mu$) separate of sediments (layers) from certain localities. Lastly, x-ray data are given for biotite, muscovite, and sericite, mica minerals which are closely related to soil clay minerals: thus, biotite to glauconite, and muscovite and sericite to illite.

In the clay separate of biotite-rich soils from Sumatra's East Coast of rhyolitic origin, kaolinite was found together with traces of biotite and of weathered

TABLE 1

Relation between the observed distance $2\,l'$ *(distance between two corresponding reflections on an x-ray photo), the real glancing angle* θ *(as degrees), and the interplanar spacing* d *(as A.) of a crystal face, assuming the order of the reflection* (n) = *1, a radius (true) of the camera* R = *27.24 mm., a radius of the specimen in the capillary* r = *0.30 mm., a real eccentricity of the specimen in the direction of the rays* b = *0.09 mm., and with Co radiation* (λ = *1.787 A.*)

$2\,l'$ IN MM. (OBSERVED)	$\theta = \frac{2\,l'}{4\,R}$ (RADIANS)	θ IN DEGREES	d IN A. (NOT CORRECTED)	$r\,(l + \cos 2\theta)$	sin. $2\,\theta$	$2\,b$ sin. $2\,\theta$	CORRECTION	$2\,l'$ IN MM. (CORRECTED)	$\theta = \frac{2\,l' \text{ cor.}}{4\,R}$ (RADIANS)	θ IN DEGREES)	d IN A. (CORRECTED)
4.0	0.0367	2.1028	24.3	0.60	0.0733	0.01	0.59	3.41	0.0313	1.7934	28.5
4.1	0.0376	2.1543	23.8	0.60	0.0751	0.01	0.59	3.51	0.0322	1.8449	27.7
4.2	0.0385	2.2059	23.2	0.60	0.0769	0.01	0.59	3.61	0.0331	1.8965	27.0
40.0	0.3671	21.0333	2.49	0.52	0.6700	0.12	0.40	39.60	0.3634	20.8213	2.51
40.2	0.3689	21.1364	2.48	0.52	0.6727	0.12	0.40	39.80	0.3653	20.9301	2.50
40.0	0.3708	21.2453	2.47	0.52	0.6755	0.12	0.40	40.00	0.3671	21.0333	2.49
80.0	0.7342	42.0666	1.33	0.33	0.9948	0.17	0.16	79.84	0.7327	41.9806	1.34
80.5	0.7388	42.3301	1.33	0.33	0.9957	0.17	0.16	80.34	0.7373	42.2442	1.33
81.0	0.7434	42.5937	1.32	0.33	0.9965	0.17	0.16	80.84	0.7419	42.5077	1.32
139.0	1.2757	73.0922	0.93	0.05	0.5565	0.10	−0.05	139.05	1.2762	73.1200	0.93
139.5	1.2803	73.3558	0.93	0.05	0.5488	0.09	−0.04	139.54	1.2807	73.3787	0.93
140.0	1.2849	73.6193	0.93	0.05	0.5411	0.09	−0.04	140.04	1.2852	73.6365	0.93

biotite. Here, weathering is so intense that the coarse biotite particles are converted first to hydrated biotite—$(K, OH_3)(H_2, Mg, Fe)_3(Si_3Al)O_{10}(OH)_2 \cdot nH_2O$—and then to kaolinite.

Hydrated biotite can be distinguished from biotite—$K(Mg,Fe)_3(Si_3Al)O_{10}(OH)_2$—only by a larger basal spacing, that is, $d = 13.6\text{–}13.8$ A. against $d = 10.9$ A. (pl. 3, fig. 24).

Hydrated biotite formed by weathering of coarse biotite particles is, of course, quite different from the coarse mixed layer mineral consisting of a stacking of three vermiculite—$(Mg,Fe)_3(Si,Al,Fe)_4O_{10}(OH)_2 \cdot 4H_2O$—to two biotite units per unit cell, as was observed by Gruner (12) and which he called "hydrobiotite."

The following reflections are characteristic and serve to distinguish vermiculite, biotite, and hydrated biotite from one another:

Vermiculite: $d = 4.64$ A. and $d = 3.60$ A.

Vermiculite + glycerol: $d = 3.60$ A. as vermiculite, but reflection $d = 4.64$ A. absent and new reflections on the photo: $d = 4.80$ A. and $d = 4.16$ A.

Biotite and hydrated biotite: $d = 3.36$ A. and reflections of both minerals unchanged or new reflections unaffected by glycerol or potassium.

Biotite: $d = 10.9$ A. against $d = 13.6\text{–}13.8$ A. for hydrated biotite, $d = 14.9\text{–}17.6$ A. (broad band) for vermiculite with or without glycerol, and $d = 11.5\text{–}12.4$ A. (variable) for vermiculite saturated with potassium.

Older literature commonly reports that muscovite is found in the $<2\mu$ separate of soils, sometimes in considerable amounts. Muscovite, however, is a mineral present in volcanic rocks, that is, a "primary" mineral which cannot withstand weathering as particles $<2\mu$, in contrast with specific clay minerals, that is, "secondary" minerals. Therefore, most of the muscovite found in the $<2\mu$ separate of soils, except for some larger, flat-shaped muscovite which has sedimented together with particles $<2\mu$, is in reality illite (also called "hydromuscovite," "sericite-like mineral," and "glimmerton").

The difference between the two minerals is small. Only the following reflections on the photos are characteristic and serve to distinguish one from the other:

	distinct lines			diffuse band	
Illite:	$d = 3.03$ A.,	$d = 2.82$ A.	and	$d = 1.68$ A.,	$d = 1.64$ A.

	distinct lines			distinct lines	
Muscovite:	$d = 3.19$ A.,	$d = 2.97$ A.	and	$d = 1.74$ A.,	$d = 1.64$ A.

If, however, illite and muscovite both occur in the $<2\mu$ separate of a sediment, they can only be distinguished thus:

Illite: $d = 3.03$ A. and $d = 2.82$ A.
Muscovite: $d = 3.19$ A. and $d = 2.97$ A.

Sometimes in the clay separate of soils, especially in the finer separates ($<0.5\ \mu$, $<0.125\ \mu$), $d = 3.03$ A. and $d = 2.82$ A. of illite are barely visible. Bright lines appear, however, if these separates are pretreated with 10 per cent HCl for 1 hour on a boiling water bath and are then treated with 5 per cent NaOH for 10 minutes at approximately 55° C. to dissolve precipitated silica.

Exceptions to the rule that only "secondary" minerals occur as particles $<2\ \mu$ in soils are quartz and cristobalite, which are extremely resistant to weathering processes. Thus quartz, even when leached with organic acids (podzol weathering process) is virtually unaffected (34). Quartz and cristobalite, therefore, may occur in considerable amounts in the $<2\ \mu$ separate of sediments, as was encountered in some thoroughly weathered Brazilian soil clays, which contained approximately 50 per cent quartz, and as was observed by Gruner (15) in some thoroughly weathered volcanic ash beds, which contained approximately 30 per cent cristobalite.

Iron and aluminum oxides (goethite, hematite, hydrargillite, boehmite) and calcite, which are readily influenced by weathering processes, are also exceptions. Thus, in the tropics, yellow-colored (goethite) profiles in fresh excavations of a road become red colored (hematite) after some years if the soil is well drained and air can enter it readily. In river and sea muds, fine ($<2\ \mu$) calcite particles may be formed by microbiological activity. In sea muds, moreover, fine calcite particles may be precipitated by changes of the CO_2 percentage caused by variations in the temperature of the sea water.

Among the "secondary" minerals, metahalloysite (7 A.) may confuse the identification of kaolinite, as metahalloysite, with its characteristic broad diffuse band of 2.6–2.3 A., causes the distinct 2.57–2.49 A. and 2.34–2.28 A. reflections of kaolinite also to appear on the photo as a broad diffuse band. Thus kaolinite, when occurring together with fresh crystallized metahalloysite, such as was found in some lateritic weathered soils from Sumatra, may be mistaken for metahalloysite. Heating the clay separate with 10 per cent HCl for 1 hour on a boiling water bath and then dissolving the precipitated silica by treatment with 5 per cent NaOH for 10 minutes at approximately 55° C., will readily remove this disturbing component.

X-RAYS

X-rays were obtained by a Philips Co target, water-cooled, having an output of ±19 ma. at ±40 KV, and producing $K_{\alpha\text{-}1} = 1.78529$ A., $K_{\alpha\text{-}2} = 1.78919$ A., and $K_{\beta\text{-}1} = 1.61744$ A. rays. The intensity of the last were reduced to almost negligible amounts by means of an Fe filter (0.015 mm.), which was placed before the opening (of Lindemann glass) of the Co target. In this way, almost nothing but $K_{\alpha\text{-}1}$ and $K_{\alpha\text{-}2}$ rays entered the camera in amounts of 2:1 (average = 1.787 A.). A Co target was used to obtain clear photos of clay minerals which may contain considerable amounts of iron ions in their crystals (hematite, goethite, nontronite) or which, like most clay particles separated from soils, are contaminated by iron and manganese oxides (hydroxides).

CAMERA

A hydrogen-filled cylindrical Favejee camera (10) having an inner diameter of 54.9 mm. was used. Width and length of the film were respectively 150 and 45 mm. A collimator with 0.5-mm. pinholes spaced 55 mm. apart was used.

The clay specimen turned at about six rotations an hour in a thin-walled glass capillary with a diameter of 0.6 mm. and which was mounted at the lower end of a glass tube (diameter = 10 mm.) by means of solid wax like that commonly used by dentists. It was centered in the camera, with regard to the axis of rotation of the specimen, by means of two screws which could move the glass tubes at right angles to each other. This manipulation was controlled by means of a microscope (25×) which could be moved some distance into the camera and by placing a lamp at the opposite opening of the camera.[2]

The average time of exposure was 8 hours. Blue-Brand Eastman x-ray films duplitized and Kodak developer and fixer were used. Development was performed under standardized conditions. To determine shrinkage, a scale was printed on the film before the camera was loaded. Shrinkage, however, proved to be so small with this sized camera, that it could be neglected.

With this arrangement, x-ray diffraction patterns could be obtained that were still bright at the center of the film hole (with a diameter of 4 mm.). Thus spacings up to approximately 26 A. could be correctly read off. A disadvantage of this small camera is that its dispersing power is too low to give distinct lines of reflections very close to each other. X-ray diffraction photos of soil clay minerals $<2\ \mu$ are generally not sharp anyway, as most of the lines are broadened as a result of disturbed faces occurring at the surfaces of the fine particles. Furthermore, colloids cause some darkening, especially in the center of the film, where are found the most important reflections by which the soil clay minerals can be distinguished from one another. These colloids can, of course, be removed by the Drosdoff method (7), but this manipulation also removes goethite, boehmite, and calcite.

To obtain more detailed x-ray data which may be important for identification of a certain clay mineral occurring together with other clay minerals, or to determine the real crystal system to which a certain clay mineral belongs, one should of course operate with a camera of larger dispersing power. This was done successfully by Brindley (5) for kaolinite and by P. M. de Wolff for halloysite (10 A.), metahalloysite, attapulgite, montmorillonite, and glauconite.[3] A disadvantage of cameras with large dispersing power is that faint lines are broadened in such a way that they mostly disappear in the general background darkening of the film.

PREPARATION OF THE SAMPLE

The $<2\ \mu$ particles were separated, by means of Atterberg sedimentation cylinders, from the natural clays and soils by use of 10 per cent H_2O_2 to destroy organic matter and of 0.1 N NH_4OH to disperse the particles. After being dried at approximately 110° C., they were passed through a 45-μ sieve. The material thus obtained was inserted in the 0.6-mm. glass capillary by carefully tapping the tube to which the capillary was fastened.

To obtain constant x-ray data of minerals with basal spacings varying considerably with the amount of water between the layers, these clays were also glycerol-treated according to the MacEwan method (30). For this purpose, the dried clay particles $<2\ \mu$ obtained by the Atterberg sedimentation cylinders were first soaked with glycerol and then heated at approximately 170° C. in an oven until they were dry enough to pass through the 45-μ sieve. The sieved material was put into the capillary, and the glass tube was closed at the top with a rubber stopper.

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[2] For further details, see (10).

[3] Unpublished results.

READINGS

The distances between corresponding reflections on the photo were determined with a measuring microscope especially constructed for the size of the films obtained with the Favejee camera (15 by 4 cm.). White diffuse light of room temperature was produced by throwing the beams of two 40-watt Philips fluorescent mercury gas tubes through a plate of opaque glass. The film was mounted and held flat on this plate by means of a spring clamp on each side.

The microscope had a 30-mm. objective and an eyepiece with a vertically mounted wire in the middle. Its magnification amounted to about 6 ×, which was sufficient for examination of the large-grained x-ray films, upon which, besides bright lines, more diffuse lines (bands) were produced by the diffracted x-rays of the clay mineral.

The microscope tube was moved slowly alongside the film by means of a reduction gear, so that very accurate observations could be read on the scale. The latter was machine-divided into millimeters, and the vernier permitted readings to 0.1 mm. Relative intensities were noted by visual observation and expressed in grades: I = very strong, II = strong, III = medium, IV = weak, V = very weak, VI = barely visible.

CALCULATIONS

Correction for thickness of specimen in thin-walled glass capillary

In figure 1 the path of a beam in the circular camera, diffracted on the surface of the specimen, is shown schematically. From this it can be concluded that a correction of $r(1 + \cos. 2\,\theta)$, according to Kolkmeyer *et al.* (25), must be introduced into the calculation to obtain the real d (interplanar spacing) value of a diffracted beam if the distance between the most intensive parts is measured. Especially at low glancing angles, the correction for thickness of the specimen may be considerable (table 1).

In the foregoing, it has been assumed that the beam is diffracted only on the surface of the specimen. If, however, the beam passes through the specimen and if only the distance between the most intensive parts of the corresponding lines on each side of the center of the film hole is measured, the correction for thickness of the specimen should, of course, be omitted.

To determine what happens in the camera using a Co tube ($K_{\alpha-1\alpha-2}$ = 1.787 A.) the following calculations are suggested:

Absorption of x-rays by material can be represented by the equation

$$I = I_0 e^{(\mu/\rho)\,pd}$$

where I = intensity of x-rays after penetrating the material to a certain depth
I_0 = intensity of x-rays at the surface
e = 2,718281 . . .
$\frac{\mu}{\rho}$ = mass absorption coefficient per centimeter material [For these coefficients, see Hodgman (19, pp. 2006, 2007).]
d = volume weight of the material
p = depth, in centimeters, to which the x-rays have penetrated the material.

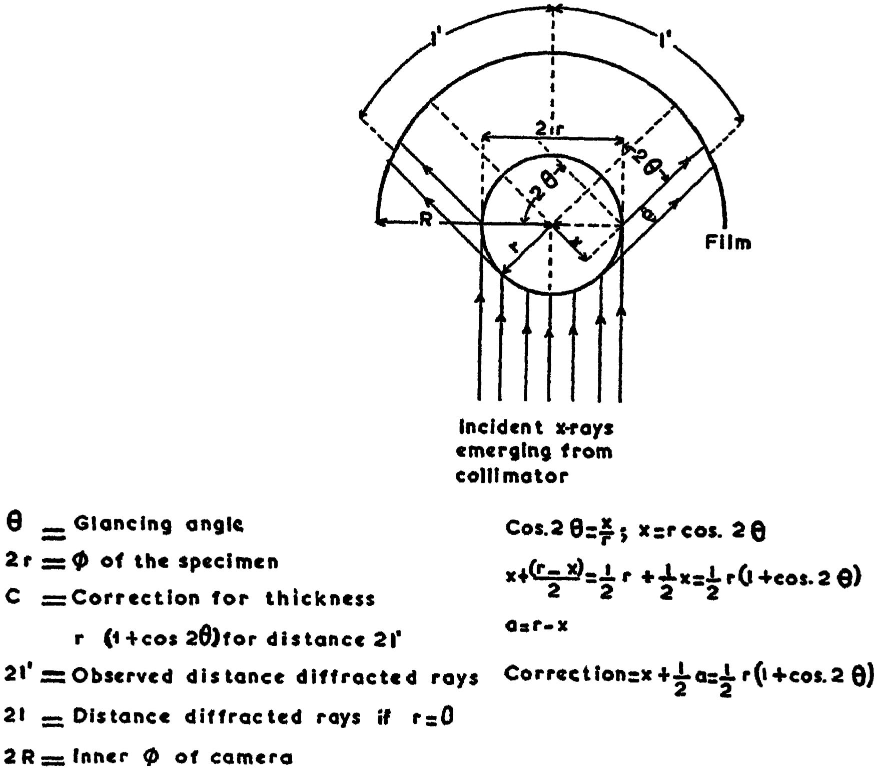

1'
1'
2 r
2θ
2θ
θ
R
r
Film
Incident x-rays emerging from collimator
θ = Glancing angle
2r = ϕ of the specimen
C = Correction for thickness r (1+cos 2θ) for distance 2l'
2l' = Observed distance diffracted rays
2l = Distance diffracted rays if r=0
2R = Inner ϕ of camera
Cos.2θ = x/r ; x = r cos. 2θ
x + (r − x)/2 = 1/2 r + 1/2 x = 1/2 r(1 + cos. 2θ)
a = r − x
Correction = x + 1/2 a = 1/2 r(1 + cos. 2θ)

FIG. 1. CALCULATION OF CORRECTION FOR DIFFRACTED RAYS CAUSED BY THICKNESS OF SPECIMEN

Not drawn to scale.

In table 2 the results are summarized for several clay minerals and other material when the volume weight of the powdered material in the capillary is assumed to be 0.5–1.0 and the inner diameter of the capillary or that of the massive rod equals 0.06 cm. From these results it may be concluded that the incident x-rays are almost completely absorbed by heavy minerals such as platinum Only 0.1 and 3.8 per cent of the incoming x-rays go through sodium chloride in the capillary. More go through clay minerals, especially montmorillonite saturated with water (or glycerol). But these figures can also be disregarded, in view of the fact that montmorillonite generally contains considerable amounts of magnesium and calcium having a μ/ρ of approximately 60 and 225 respectively.

As regards cellulose, 70 per cent pass through the specimen with a diameter of 0.06 cm. In this case the correction for thickness of the specimen (maximum = 0.06 cm.) may, of course, be omitted.

Correction for eccentricity of specimen with regard to center of camera

In figure 2 the path of a beam in the circular camera is shown schematically. The following positions are noted: The center of the specimen is found on the left (see B) or right (see A) side of the center of the camera cylinder. From figure 2 A and 2 B it may be concluded that the distances observed (2 l') are not influenced by the position of the center of the specimen with regard to the center of the camera cylinder. If the divergence is too large, however, the photo is darker (overexposured) at one side than at the other (underexposured), and accurate readings cannot be obtained.

TABLE 2

Absorption of $K_{\alpha 1-\alpha 2}$ *Co radiation* (λ = *1.787 A.) by specimens 0.06 cm. thick and having a volume weight of 0.5 and 1.0*

MATERIAL	FORMULA	$\frac{\mu}{\rho}$	SPECIFIC GRAVITY	VOLUME WEIGHT	$\frac{I}{I_0}$	VOLUME WEIGHT	$\frac{I}{I_0}$
					per cent		*per cent*
Platinum......	Pt	280	11.9	11.9*	10^{-87}		
Cellulose......	$(C_6H_{10}O_5)n$	12	1.5	0.5	70		
Quartz........	SiO_2	52	2.6	0.5	21	1.0	4.4
Sodium chloride.........	NaCl	109	2.2	0.5	3.8	1.0	0.1
Kaolinite......	$(Al_2)Si_2O_5(OH)_4$	46	2.6	0.5	25	1.0	6.3
Montmorillonite.......	$(Al_2)Si_4O_{10}(OH)_2 \cdot nH_2O$	38†	2.6	0.5	28	1.0	8.0
Muscovite.....	$K(Al_2)\ (Si_3Al)O_{10}(OH)_2$	65	2.6	0.5	14	1.0	2.0

* Specimen as massive rod.

† Montmorillonite saturated with water—about 30 per cent H_2O.

From figure 2 C and 2 D it may be concluded that if the axis on which the specimen is rotated during exposure in the camera-cylinder is not exactly in the center of the camera, the distance (R') from the center of the specimen (M') to the middle of the double sensitive film is not equal to the distance (R) from the center of the camera (M) to the middle of the double sensitive film. According to Kolkmeyer and Moesveld (25), this divergence can be represented by the equation $\pm 2\ b$ sin. $2\ \theta$, if the distance between the most intensive parts of the corresponding lines on each side of the center of the film hole is measured. In this equation, b = the component of the real eccentricity of the specimen in the cylindrical camera (distance between the center of the camera and the center of the specimen) in the direction of the incident x-rays, and θ = the glancing angle of a diffracted ray.

Real glancing angle of a diffracted ray needed for calculation of interatomic spacings

An x-ray pattern was made of chemically pure KCl, of which the length of a unit cell (a_0) is known to be 6.28 A. [see, for example, Wyckoff (48)]. Thereafter,

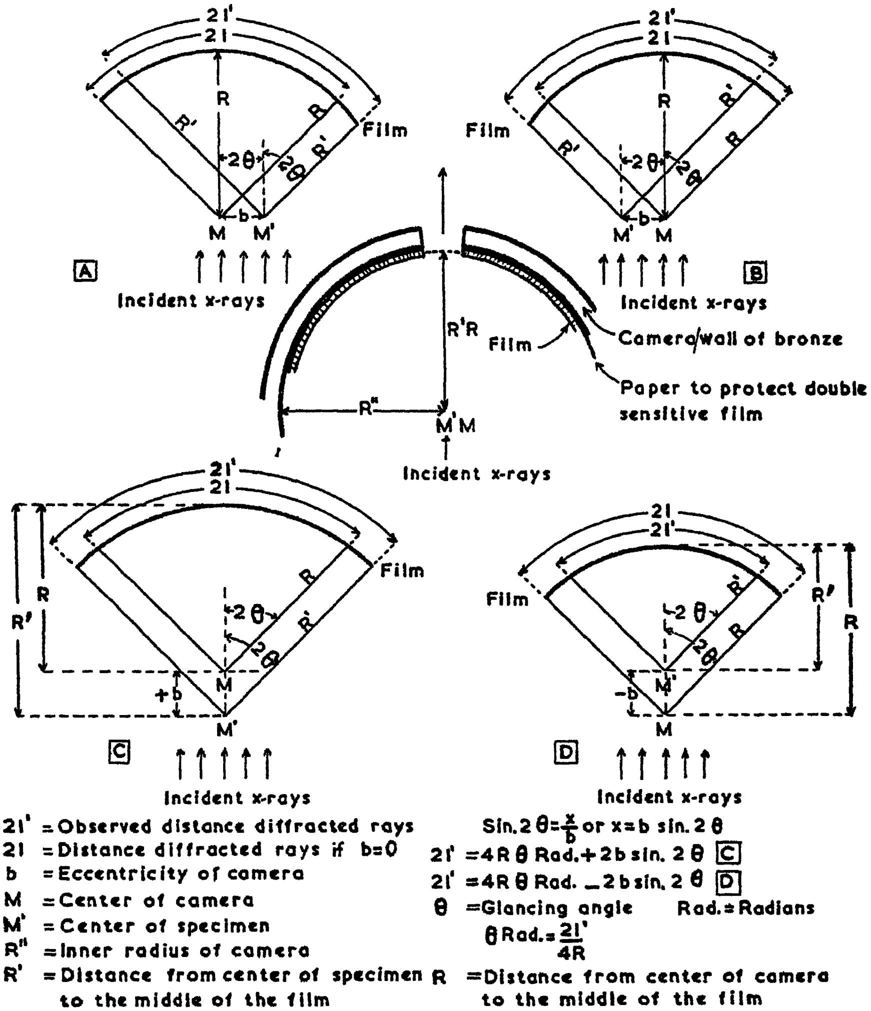

2l'
2l
R
R'
Film
2θ
b
M
M'
A
B
C
D
Incident x-rays
Camera wall of bronze
Paper to protect double sensitive film
R'R
R''
+b
-b
2l' = Observed distance diffracted rays
2l = Distance diffracted rays if b=0
b = Eccentricity of camera
M = Center of camera
M' = Center of specimen
R'' = Inner radius of camera
R' = Distance from center of specimen to the middle of the film
Sin. 2θ = x/b or x = b sin. 2θ
2l' = 4R θ Rad. + 2b sin. 2θ C
2l' = 4R θ Rad. − 2b sin. 2θ D
θ = Glancing angle
Rad. = Radians
θ Rad. = 2l'/4R
R = Distance from center of camera to the middle of the film

FIG. 2. CALCULATION OF CORRECTION FOR DIFFRACTED RAYS CAUSED BY ECCENTRICITY OF SPECIMEN WITH REGARD TO CENTER OF CAMERA

Not drawn to scale.

R and *b* were calculated from the reflections by the method of least squares, as indicated in appendix 1. The results are: $R = 27.24$ mm. ± 0.04 mm., and $b = -0.09$ mm. ± 0.08 mm.

To tell directly from the observed distances ($2\,l'$) of a photo, the corresponding

d (interatomic spacing) data, assuming n (order of reflection) = 1, a table was calculated by means of the formulas: θ (in radians) = $(2\ l'\ [\text{corrected}]/4\ R)$ and $d = (n\lambda/2 \sin. \theta)$ in which λ = the wave length of the x-rays used = 1.787 A., and θ = the glancing angle of a diffracted ray. By correcting the observed distance $2\ l'$ for the thickness of the specimen = $r\ (1 + \cos.\ 2\ \theta)$ and for the eccentricity of the specimen in the direction of the rays = $2b \sin.\ 2\ \theta$, $2\ l'$ corrected, in mm., was obtained. Table 1 gives examples of these calculations for observed $2\ l'$ values ranging from 4 mm. to 140 mm.

RESULTS

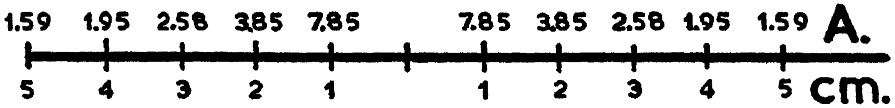
The results of the observations are summarized in three groups. Reflections observed by other investigators can be found in the literature as indicated for each mineral. As has been mentioned, differences may occur for which several factors are responsible. X-ray photos are reproduced for all the minerals investigated (plates 1 to 3) and also for the clay ($<2\ \mu$) separate of some interesting soils from different localities (plate 4).

Group I. Minerals which may occur in the clay ($<2\ \mu$) separate of soils (see appendix 2).

Quartz: α SiO_2 (1, 9, 10, 16, 18, 39, 45). ✓
Montmorillonite: $(Al)_2\ Si_4O_{10}(OH)_2 \cdot nH_2O$ (9, 14, 16, 20, 23, 24, 28, 29, 33, 39, 45).
Kaolinite: $(Al_2)\ Si_2O_5\ (OH)_4$ (5, 6, 9, 16, 35, 39, 42, 45).
Metahalloysite 7 A: $(Al)_2Si_2O_5\ (OH)_4$ (6, 27, 35, 39, 42, 43, 45).
Illite: $K(Al)_2(Si_3Al)(O,OH)_{10}\ (OH)_2$ (11, 32, 39).
Glauconite: $K_2\ (Mg, Fe^{++})_3\ (Fe^{+++}, Al)_6\ (Si_{14}Al_2)O_{40}(OH)_8$ (13, 32).
Goethite: α $FeO\ (OH)$ (1, 16, 39).
Hematite: α Fe_2O_3 (16, 17, 39).
Boehmite: γ $AlO(OH)$ (1, 16, 39, 41, 47).
Hydrargillite (gibbsite): γ $Al(OH)_3$ (1, 2, 16, 17, 39, 47).
Calcite: $CaCO_3$ (16, 18, 37).

Group II. Minerals which may occur in the clay ($<2\ \mu$) separate of sediments (layers) of certain localities (see appendix 2).

Nontronite (chloropal): $(Fe,Al)_2\ Si_4O_{10}(OH)_2 \cdot nH_2O$ (1, 14, 23, 39, 40, 45). Localities: St. Andreasberg (Germany), Castle Rock (Washington, U. S. A.), etc.
Critobalite (βSiO_2) (3, 15, 16, 21, 31, 39, 46). Localities: together with montmorillonite in some bentonites of Wyoming (U. S. A.) and of Tomesti (Rumania), etc.



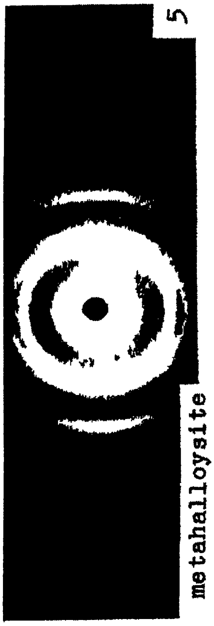
Scale of x-ray Plates

PLATES 1-3. CLAY ($<2\mu$) SEPARATE OF PURE MINERALS

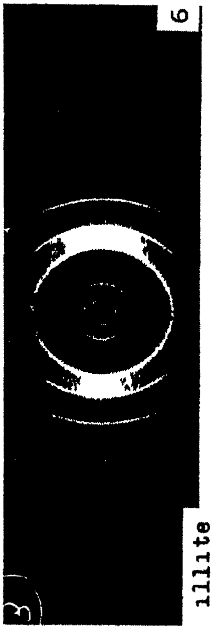
FIG. 1-13. Minerals which may occur in the clay ($<2\mu$) separate of soils

FIGS. 14-20. Minerals which may occur in the clay ($<2\mu$) separate of sediments (layers) of certain localities

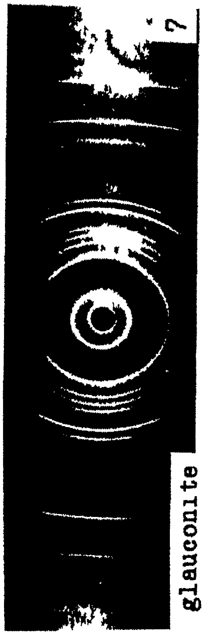
FIGS. 21-24. Rock minerals to which minerals occurring in the clay ($<2\mu$) separate of soils are closely related



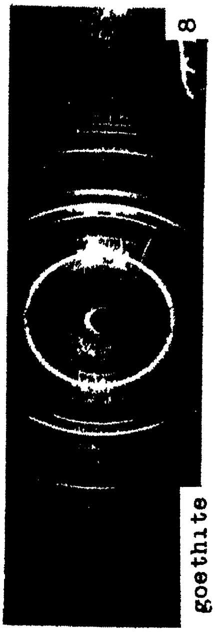
5 metahalloysite



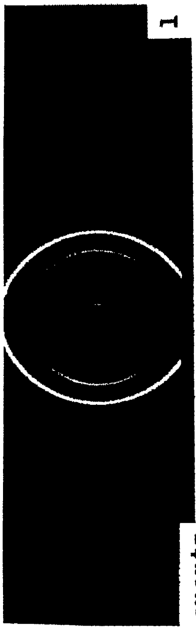
6 illite



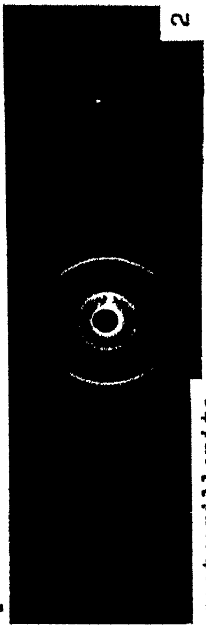
7 glauconite



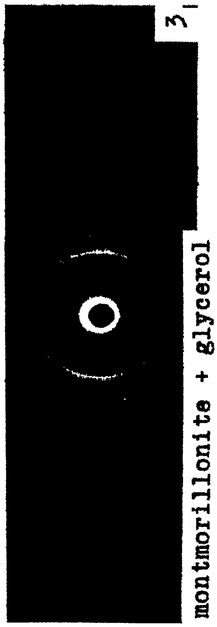
8 goethite



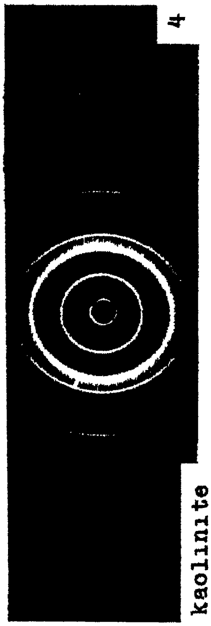
1 quartz



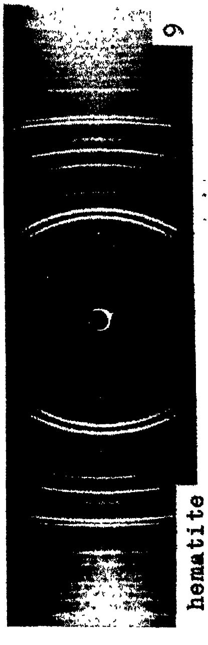
2 montmorillonite

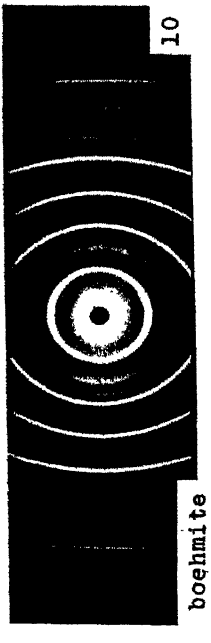


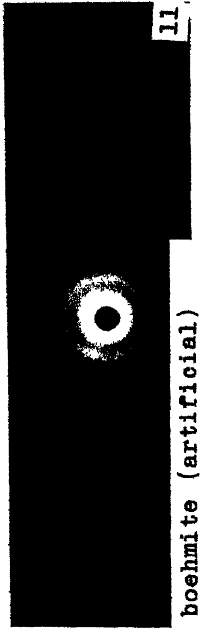
3 montmorillonite + glycerol

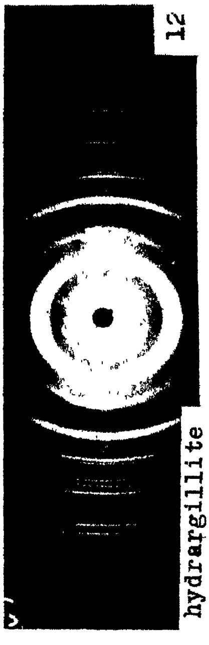


4 kaolinite

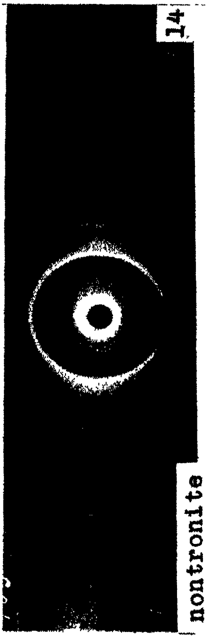

9 hematite

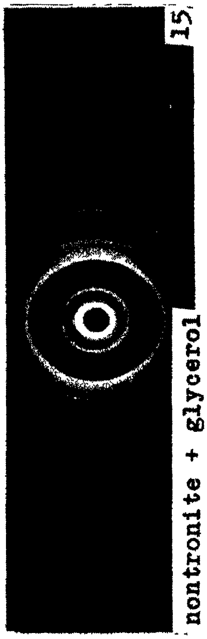

10 boehmite

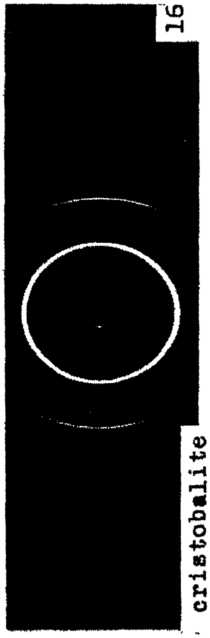

11 boehmite (artificial)

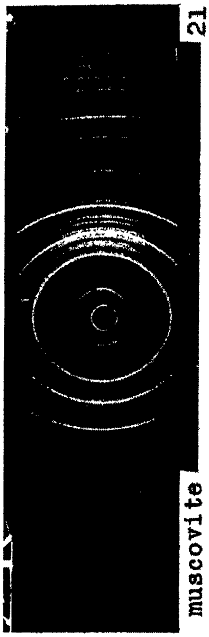

12 hydrargillite

13 calcite


14 nontronite

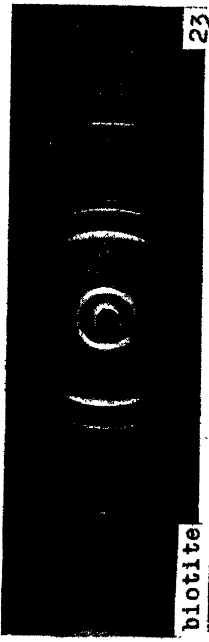

15 nontronite + glycerol


16 cristobalite

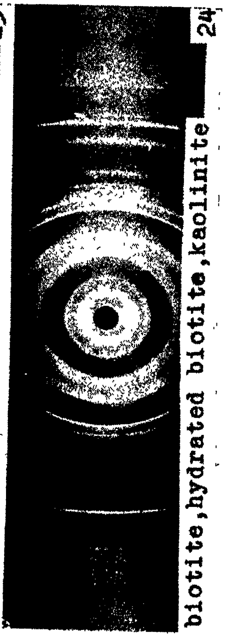


21 muscovite

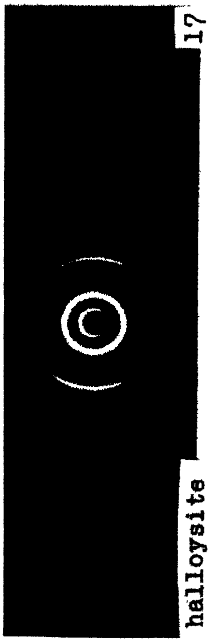
22 sericite



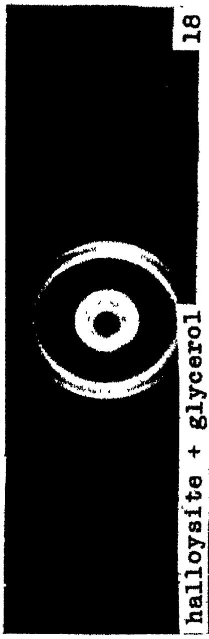
23 biotite



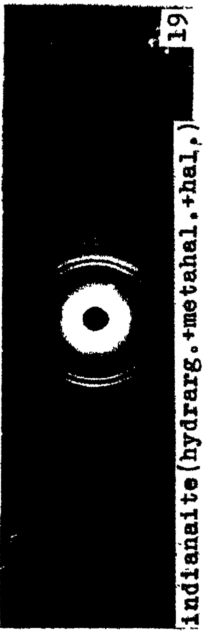
24 biotite,hydrated biotite,kaolinite



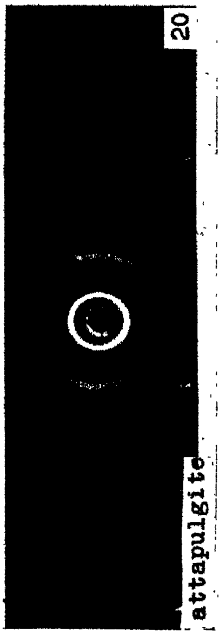
17 halloysite



18 halloysite + glycerol



19 indianaite (hydrarg.+metahal.+hal.)



20 attapulgite

Halloysite 10 A. (endellite): $(Al)_2Si_2O_5(OH)_4 \cdot H_2O$ (35, 43). Localities: Martinsberg (Hungary), Eureka (Utah, U. S. A), Djebel Debar (Libya, North Africa), etc.

Indianaite (a mixture of hydrargillite with halloysite and metahalloysite or of metahalloysite with halloysite) (44). Locality: Indiana (U. S. A.).

Attapulgite (fuller's earth, palygorskite): $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$ (4, 23, 26, 39, 45). Localities Attapulgus (Georgia, U. S. A.), Mormoiron (Vaucluse, France), etc.

Group III. Rock minerals to which minerals occurring in the clay ($<2\ \mu$) separate of soils are related (see appendix 3).

Muscovite: $K(Al)_2(Si,Al)O_{10}(OH)_2$ (1, 8, 9, 11, 16, 22, 32, 38, 45) related to sericite and illite.

Sericite: $(H,K)_2O \cdot 2SiO_2 \cdot Al_2O_3$ (38) related to muscovite and to illite.

Biotite: $K(Mg,Fe)_3(Si,Al)O_{10}(OH)_2$ (7, 13, 32, 36, 38) related to hydrated biotite and to glauconite.

APPENDIX 1

Calculation of the component of the real eccentricity of the specimen in the cylindrical camera (distance between center of camera and center of specimen) in the direction of the incident x-rays = b and the true radius of the camera cylinder = R:

θ = glancing angle of a diffracted beam.
rad. = radians.
l' = observed distance from most intensive part of reflection to center of film.
λ = $K_{\alpha 1-\alpha 2}$ = 1.787 A
r = radius of specimen in capillary = 0.3 mm.
σ = standard deviation.
R = radius of camera cylinder.
R' = distance between the center of the specimen and the middle of the double sensitive film.
b = component of the real eccentricity of the specimen in the cylindrical camera in the direction of the incident x-ray beams.
a_0 = interatomic spacing between two equal sorted ions in KCl crystal = 6.28 A.

PLATE 4. CLAY ($<2\mu$) SEPARATE, GLYCEROL-TREATED, OF SOILS FROM DIFFERENT LOCALITIES

Characteristic reflections for identification of each mineral are shown in parentheses, and minerals are arranged in decreasing order of amounts

FIG. 25. Loess, Limburg, Netherlands: illite (10.8 A. and band 1.68–1.61 A.), quartz (1.54 A.), kaolinite (7.5 A.), and montmorillonite (broad band 23.1–17.9 A.)

FIG. 26. Sea clay, Flanders, Netherlands: illite, kaolinite, quartz, and some montmorillonite

FIG. 27. Soil from weathered marl (Gulpense krijt), Limburg, Netherlands: calcite (3.04 A.), montmorillonite, and quartz

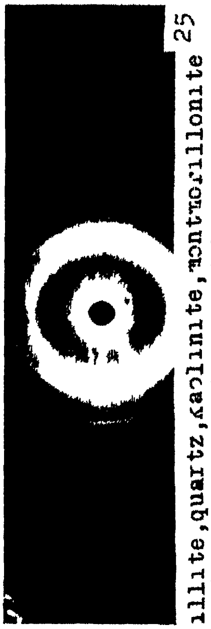
FIG. 28. Subsoil of podzol heath of Peest, Drenthe, Netherlands: illite, quartz, kaolinite, and boehmite (6.5–6.1 A.)

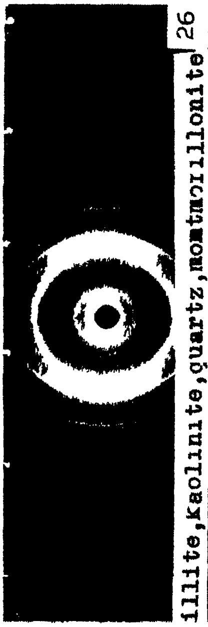
FIG. 29. Soil from weathered volcanic ash of andesitic origin, Merapi volcano, Java: montmorillonite and kaolinite

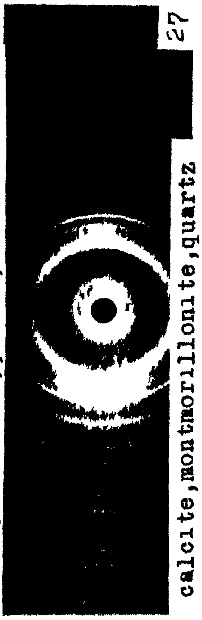
FIG. 30. Lateritic soil, terra roxa, Brazil: kaolinite, hydrargillite (5.1–4.9 A. and 4.6–4.3A), and hematite (2.70 A. and 2.51 A.)

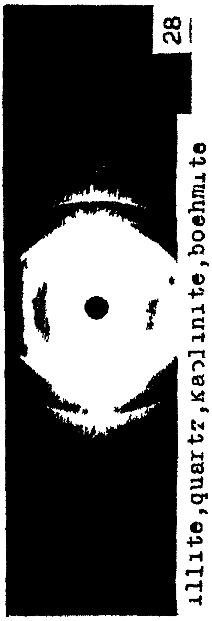
FIG. 31. Alluvial soil, Langsa, Sumatra (East Coast): kaolinite, illite, and quartz

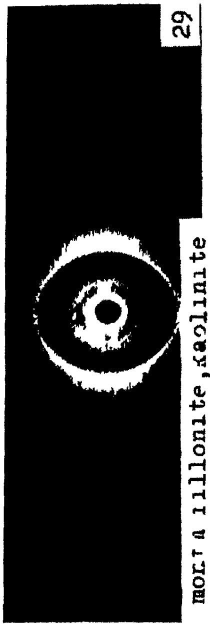
FIG. 32. Lateritic soil from weathered rhyolitic tuff, Sumatra (East Coast): kaolinite, fresh crystallized metahalloysite (broad band 2.6–2.3 A.), and some hydrargillite and quartz; metahalloysite disturbing the identification of kaolinite; the same clay when treated with HCl and NaOH consisting only of kaolinite and some quartz

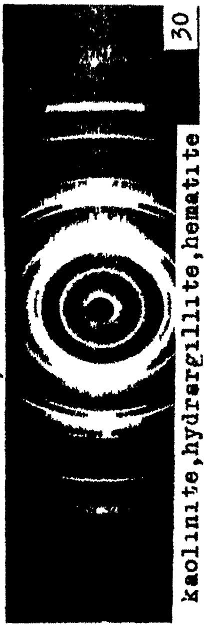

25
illite,quartz,kaolinite,montmorillonite

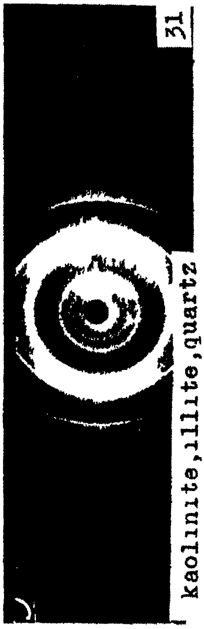

26
illite,kaolinite,quartz,montmorillonite

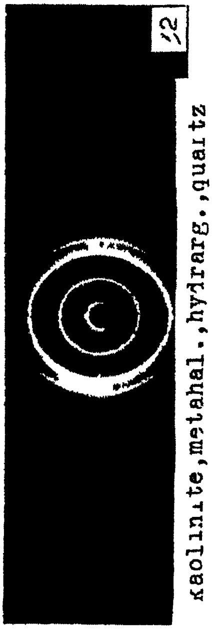

27
calcite,montmorillonite,quartz


28
illite,quartz,kaolinite,boehmite


29
montmorillonite,kaolinite


30
kaolinite,hydrargillite,hematite


31
kaolinite,illite,quartz


32
kaolinite,metahal.,hydrarg.,quartz

$2\,l'$ in mm. (observed).	31.8	45.6	56.5	66.1	75.4	84.2	102.1	111.1	121.9	134.5
h_1, h_2, h_3	200	220	222	400	420	422	440	600/442	620	622
$\sin.^2\theta \times 10^{+3}$..........	80.96	161.92	242.88	323.84	404.80	485.76	647.68	728.64	809.60	890.56
$\sin.\,\theta$	0.28453	0.40239	0.49283	0.56907	0.63624	0.69696	0.80479	0.85360	0.89978	0.94369
θ radians	0.28856	0.41412	0.51534	0.60538	0.68961	0.77116	0.93532	1.02236	1.11926	1.23362
$\frac{2\,b\,\sin.\,2\,\theta}{4\,\theta\,\text{rad.}}$	0.9454	0.8897	0.8322	0.7730	0.7118	0.6481	0.5108	0.4348	0.3507	0.2530
r. $(1 + \cos.\,2\,\theta)$	0.55	0.50	0.45	0.41	0.36	0.31	0.21	0.16	0.11	0.07
$2\,l'$ in mm. (corrected)..	31.25	45.10	56.05	65.69	75.04	83.89	101.89	110.94	121.79	134.43
$\frac{2\,l'\ \text{(corrected)}}{4\,\theta\,\text{rad.}}$	27.0741	27.2264	27.1908	27.1276	27.2038	27.1960	27.2340	27.1151	27.2032	27.2430
$\frac{x}{\theta^2}$	11.3539	5.1879	3.1336	2.1092	1.4968	1.0898	0.5839	0.4156	0.2799	0.1662
$\frac{y}{\theta^2}$	325.1486	158.7588	102.3845	74.0212	57.2036	45.7314	31.1309	25.9166	21.7150	17.9016
$x' = x - \bar{x}$	+0.1303	+0.0746	+0.0171	−0.0421	−0.1033	−0.1670	−0.3043	−0.3803	−0.04644	−0.5621
$y' = y - \bar{y}$	−0.0754	+0.0769	+0.0413	−0.0219	+0.0543	+0.0465	+0.0845	−0.0344	+0.0537	+0.0935
$\frac{x'y'}{\theta^2}$	−0.11798956	+0.03345128	+0.00265925	+0.00251577	−0.01179489	−0.01305888	−0.02939267	+0.01250408	−0.01990698	−0.03453530
$\frac{(x')^2}{\theta^2}$	0.20389973	0.03245078	0.00110104	0.00483625	0.02243853	0.04689675	0.10584841	0.13823553	0.17215647	0.20761812
$\frac{(y')^2}{\theta^2}$	0.06827638	0.03448261	0.00642262	0.00130868	0.00620003	0.00363593	0.00916195	0.00113166	0.00230191	0.00574462

$$\Sigma(h^2) = \Sigma(\text{indexes cubic crystal})^2 = \Sigma(h_1^2 + h_2^2 + h_3^2)$$

$$\sin.^2\theta = \frac{\lambda^2}{4a_0^2} \cdot \Sigma(h^2) = \frac{(1.787)^2}{4 \times (6\ 28)^2} \cdot \Sigma(h^2) = 20.24 \times 10^{-3}\Sigma(h^2).$$

$$2l' - r(1 + \cos.\ 2\theta) = 4R\theta \text{ rad.} \pm 2b \sin.\ 2\theta$$

$$R = \frac{2l' - r(l + \cos.\ 2\theta)}{4\theta \text{ rad.}} \mp \frac{2b \sin.\ 2\theta}{4\theta \text{ rad.}}$$

$$\Sigma\frac{1}{6^2} = 31.67326$$

$$\Sigma\frac{x}{\theta^2} = 25\ 8168; \qquad \bar{x} = \frac{25\ 8168}{31.67326} = 0.8151$$

$$\Sigma\frac{y}{\theta^2} = 859.9122; \qquad \bar{y} = \frac{859\ 9122}{31.67326} = 27.1495$$

$$\Sigma\frac{x'y'}{\theta^2} = -0.17554710; \qquad \Sigma\frac{x'}{\theta^2} = 0.93548161; \qquad \Sigma\frac{y'}{\theta^2} = 0.13766579$$

$$b = \frac{\Sigma\dfrac{x'y'}{\theta^2}}{\Sigma\dfrac{(x')^2}{\theta^2}} = \frac{-0.17554710}{0.93548161} = -0.187654$$

b = negative; therefore = situation D — fig. 2; thus

$$R = \bar{y} - b\bar{x} = 27.1495 + 0.187654 \times 0.8151 = 27.30246$$

$$\sigma^2 = \frac{\Sigma\dfrac{(y')^2}{\theta^2} - \Sigma\dfrac{(x'y')^2}{\theta^2}}{n-2} = \frac{0.13766579 - 0.03294216}{8} = 0.01309045$$

$$\sigma b = \pm\sqrt{\frac{\sigma^2}{\Sigma\dfrac{(x')^2}{\theta^2}}} = \pm\sqrt{\frac{0.0130945}{0.93548161}} = \pm\ 0.11829315$$

$$\sigma R = \pm\ \sigma\sqrt{\frac{1}{\Sigma\dfrac{1}{6^2}} + \frac{(\bar{x})^2}{\Sigma\dfrac{(y')^2}{\theta^2}}} = \sigma\sqrt{0.03157237 + 0.71020959}$$

$$= \pm\ 0.11441350 \times 0.86126765 = \pm\ 0.09854065$$

R = 27.30 mm. ± 0.10 mm.; b = −0.19 mm. ± 0.12 mm.

The foregoing calculations have the effect that the weight of an observation ($2\ l'$) diminishes with increasing order of $4\ \theta$. This seems reasonable, because the distance between two corresponding reflections on a x-ray photo can be more accurately measured at the lower distances than at the higher ones, as the path of the measuring microscope is going more accurately through the middle of the reflections at the lower distances than at the higher ones. As the weights of the observations according to the calculation are taken to be inversely proportional to $(\theta)^2$, however, this means that the weight of the smallest $2\ l'$ (at $\theta = 0.28056$) is 18,276 times the weight of the largest $2\ l'$ (at $\theta = 1.23362$). As this difference in weight seems too high, the calculation has been made also under the assumption that all observations have the same weight.

This method, which has been worked out by the statistical department of the Central Organization for Applied Research in the Netherlands T.N.O.—The Hague, runs as follows:

The basic relation is $2\,l' = 4\,R\,\theta + 2\,b \sin\, 2\,\theta$ where: first, $2\,l'$ is the measured distance between two corresponding reflections after correction for the thickness of the capillary; second, R is the (true) radius of the camera, and third, b is the eccentricity in the direction of the rays. The values of R and b are unknown A least-square solution for R and b is found by minimizing:

$$F = \Sigma(2\,l' - R\,\theta - 2\,b \sin\, 2\,\theta)^2$$

The equations for R and b become:

$$R: -\frac{1}{2}\frac{\delta F}{\delta R} = \Sigma 4\theta(2l' - 4R\theta - 2b \sin\, 2\theta) = 0$$

$$b: -\frac{1}{2}\frac{\delta F}{\delta b} = \Sigma 2 \sin\, 2\theta(2l' - 4R\theta - 2b \sin\, 2\theta) = 0$$

The standard deviations for R and b are found from the formulas:

$$s_R^2 \quad \frac{\Sigma(2l' - 4R\theta - 2b \sin\, \theta)^2}{n-2} \times \frac{\Sigma(\sin\, 2\theta)^2}{\Sigma(2\theta)^2\Sigma(\sin\, 2\theta)^2 - (\Sigma 2\theta \sin\, 2\theta)^2}$$

$$s_b^2 = \frac{\Sigma(2l' - 4R\theta - 2b \sin\, \theta)^2}{n-2} \times \frac{\Sigma(2\theta)^2}{\Sigma(2\theta)^2\Sigma(\sin.\, 2\theta)^2 - (\Sigma 2\theta \sin\, 2\theta)^2}$$

The values for R and b and their standard deviations calculated by this method are:

$R = 27.2377$ mm. $\sigma R = \pm 0.0406$ mm.
$b = -0.0863$ mm. $\sigma b = \pm 0.0784$ mm

Confidence intervals (fiducial limits) for R and b are to be found by multiplying the standard deviations by an appropriate value of "Student's" t; for example:

fiducial lim. $R = t - 0.05 \times \sigma R = 2.306 \times 0.0406 = \pm 0.0935$ mm.
fiducial lim. $b = t - 0.05 \times \sigma b = 2.306 \times 0.0784 = \pm 0.1807$ mm.

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APPENDIX 2

Group I: X-ray diffraction data of minerals $<2\ \mu$, which may occur in the clay separate of soils: quartz, montmorillonite, kaolinite, metahalloysite, illite, glauconite, goethite, hematite, boehmite, hydrargillite, calcite, summarized in decreasing order of their *d* spacings in A.

i = relative intensities estimated visually in grades: I = very strong, II = strong, III = medium, IV = weak, V = very weak, VI = barely visible.

d = interatomic spacings, ↕ = reflection variable, { = reflection broadened.

QUARTZ		MONTMORILLONITE		MONTMORILLONITE + GLYCEROL		KAOLINITE		METAHALLOYSITE		ILLITE		GLAUCONITE		GOETHITE		HEMATITE		BOEHMITE		BOEHMITE (ARTIFICIAL)		HYDRARGILLITE		CALCITE	
i	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*
				I	{23.1																				
		I ↑	{20.2		17.9																				
			15.6																						
		I	{15.1																						
			12.6																						
														VI	{11.1	VI	{11.1								
										I	{10.8	I	{10.9												
		I ↓	{10.3																						
				III	9.42																				
									{7.6												{8.1				
						II	{7.5	II												II					
									7.3									VI	7.27						
																		I	{6.5		6 3				
				V	6.08														6.1						
		VI	5.26	VI	5.16																		{5.1		
										V	5.01			VI	5.02							I	4.9		
						II	{4.6		{4.5			II	4.64										4.6		
		II	{4.58	II	{4.58			I		II	4.52														
III	{4.4								4.4													II			
	4.3																						4.3		
						III	4.2																		
														I	4.22			V	{4.2						
										VI	{3.88														
																								V	3.86
VI	3.7											IV	3.73												
	β															III	{3.70					VI	3.70		
				IV	3.59	II	{3.6	III	{3.6														β		
																		V	3.60						

I	3.4														V	3.40									
	3.3									II	3.34	III	3.36												
																					3.32	IV	3.34	VI	3.32
																			3.28	II					β
												IV	3.13					II				V	3.22		
																			3.15		3.15				
		V	3.10	V	3.00					V	3.03														
																		VI	3.00					I	3.04
										V	2.82	VI	2.82												
		VI	2.72	VI	2.72	VI	2.76	VI	2.76					III	2.70	I	2.70		2.70			VI	2.71		
																		VI							
		IV	2.58	IV	2.58							II	2.60	V	2.58				2.62						
						III	2.57	V	2.6	II	2.58					II	2.51							IV	2.50
III	2.46	VI	2.43	VI	2.43	III	2.49	V	2.3	V	2.46	IV	2.42	II	2.45						2.41	II	2.46		
										V	2.37								2.39			III	2.39		
																		II		III					
						III	2.34												2.35		2.34				
III	2.28	VI	2.26	VI	2.26	IV	2.28			V	2.25	V	2.28	IV	2.25							V	2.27	III	2.28
														IV	2.19	III	2.20	VI	2.20			V	2.25		
V	2.23					VI	2.19	VI	2.19	VI	2.13	V	2.18			VI	2.10					IV	2.17	III	2.10
IV	2.12									IV	2.00	V	2.01	VI	2.00			VI	2.08			II	2.05		
						V	1.99	VI	1.99									V	1.99			III	2.00		
IV	1.97					VI	1.94							V	1.92							III	1.92	II	1.92
						VI	1.89												1.88		1.90			II	1.87
																		I		I					
II	1.82											VI	1.85	V	1.80	III	1.84		1.85		1.84	II	1.80		
						VI	1.78					VI	1.74					V	1.78			II	1 74		
		V	1.70	V	1.70									III	1.71			VI	1.71						
						VI	1.69			VI	1.68			VI	1.68	II	1.69					II	1.08		
IV	1.66	VI	1.60	VI	1.60	IV	1.66	V	1.67	IV	1.64	IV	1.66	VI	1.65			III	1.66	VI	1.66	VI	1.66		
						VI	1.62	VI	1.64															VI	1.62
		VI	1.59	VI	1.59							VI	1.61	VI	1.60	IV	1.60							IV	1.60
						VI	1.58							IV	1.56							V	1.58		
II	1.54	III	1.50	III	1.50	V	1.54											V	1.53						1.52
																								IV	
						III	1.48	III	1.48	III	1.50	II	1.51	IV	1.51	III	1.49	VI	1.50			VI	1.49		1.51
IV	1.45					VI	1.46					VI	1.43	IV	1.46	III	1.45	IV	1.46			II	1.46	VI	1.47
V	1.42													VI	1.42			V	1.44	II	1.45	VI	1.44	V	1.44
						VI	1.39															II	1.41	V	1.42
II	1.37					VI	1.37					VI	1.38	VI	1.39			V	1.38			VI	1.37	VI	1.36
						VI	1.34			VI	1.34	VI	1.34	VI	1.36	VI	1.35	VI	1.35			V	1.36	V	1.34
												IV	1.31	V	1.32	IV	1.31	III	1.31	IV	1.31	V	1.32		

APPENDIX 2—*Continued*

QUARTZ		MONTMORILLONITE		MONTMORILLONITE + GLYCEROL		KAOLINITE		METAHALLOYSITE		ILLITE		GLAUCONITE		GOETHITE		HEMATITE		BOEHMITE		BOEHMITE (ARTIFICIAL)		HYDRARGILLITE		CALCITE	
i	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*
IV	1.29	V	{ 1.29	V	{ 1.29	V	1.30			V	1.29	VI	1.29	VI	1.29							V	1.30	V	1.29
						V	1.28	V	{ 1.28													VI	1.27		
IV	1.25	V	1.25	V	1.25	VI	1.26					VI	1 26	VI	1.26	V	1.26					V	1.25	VI	1.25
						V	{ 1.23	V	{ 1.23	VI	1.24			VI	1.24	VI	1.23					VI	1.23	V	1.24
V	1.22															VI	1.22	VI	1.22						
												VI	1.21	VI	1.20			VI	1.21			IV	1.21		
III	1.19			VI	1.19	VI	1.19	VI	1.19							V	1.19					V	1.19		
III	1.18					VI	1.17									V	1.17					VI	1.18	V	1.18
V	1.15					VI	1.15	VI	1.15															IV	1.15
														VI	{ 1.14	IV	1.14					V	{ 1.14	VI	1.14
		VI	1.12	VI	1.12									V	1.12							V	1.12		
								VI	1.10							IV	1.10					VI	1.11		
																						VI	1.09		
VI	1.08							VI	1.08							VI	1.08					V	1.08		
VI	1.06																							VI	1.06
V	{ 1.05															IV	1.05							IV	1.05
V	1.03	VI	1.02	VI	1.02			VI	1.02							V	1.04							V	1.03
V	1.01															V	0.99							IV	1.01
V	0.99	VI	0.98	VI	0.98											VI	0.97							VI	0.98
																IV	0.96							VI	0.97
																V	0.95							V	0.96
																								VI	0.94

Group II: X-ray diffraction data of minerals which may occur in the clay ($< 2\,\mu$) separate of sediments (layers) of certain localities: nontronite, cristobalite, halloysite 10 A., indianaite, attapulgite, summarized in decreasing order of their *d* spacings in A.

Group III X-ray diffraction data of rock minerals: muscovite, sericite, and biotite o which mineral occurring in the clay 2 separat of soils are closely related, summarized in decreasing order of their *d* spacings in A.

NONTRONITE		NONTRONITE + GLYCEROL		CRISTOBALITE		HALLOYSITE		HALLOYSITE + GLYCEROL		INDIANAITE				ATTAPULGITE		MUSCOVITE		SERICITE		BIOTITE	
										Metahalloysite + Halloysite		Hydrargillite + Metahalloysite + Halloysite									
i	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*
		I	23.1																		
			17.9																		
I	18.8																				
	15.6																				
								I	12.6												
														I	12.0						
									11.4												
																II	10.9	III	10.8	I	10.9
						I	10.8			VI	10.8	V	10.8		10.6						
		III	9.52							IV	7.4	V	7.4								
		VI	6.10											V	6.61						
														V	5.59						
VI	5.29	VI	5.18																		
												II	5.0	III		VI	5.01	V	5.01		
															4.60					V	4.64
II	4.66	II	4.66	VI	4.5	II	4.5	II	4.5			I	4.5			IV	4.50	II	4.50		
							4.4		4.4	II	4.4		4.3	IV	4.30						
				I	4.2																
					4.0																
																V	3.91				
																		VI	3.8	VI	3.85
								III	3.72					V	3.72						
																V	3.73				
		IV	3.61			VI	3.6			III	3.60	IV	3.60								
						IV	3.4													VI	3.57
																V	3.48	VI	3.48		
												V	3.34	IV	3.40	II	3.34	IV	3.34	III	3.36
												VI	3.22	IV	3.22	VI	3.19	VI	3.19		

V	3.12			III	3.15															VI	3.16
		V	3.02											VI	3.00					VI	3.03
																V	2.97	V	2.97	VI	2.92
				III	2.86											V	2.87	V	2.87		
						VI	2.76	VI	2.76			VI	2.71			VI	2.79		2.79	VI	2.82
IV	2.63	IV	2.63							V	2.6			IV	2.61					II	2.63
						IV	2.57	IV	2.57			VI	2.57	IV	2.52	II	2.58	I	2.53	VI	2.52
VI	2.46	VI	2.46	II	2.49							IV	2.46			V	2.47	VI	2.47	III	2.46
VI	2.30	VI	2.30	VI	2.34	IV	2.37	IV	2.37	V	2.3	IV	2.39	VI	2.35	V	2.38	VI	2.38		
				VI	2.23							VI	2.27			V	2.26	VI	2.25	VI	2.27
						VI	2.19	VI	2.19			VI	2.17				2.20			IV	2.18
				V	2.12									V	2.15	III	2.13	IV	2.13	VI	2.12
				V	2.02							V	2.05			VI	2.03	VI	2.03	VI	2.04
						VI	1.99	VI	1.99	VI	2.00	V	2.00	VI	2.00	III	2.00	IV	2.00	IV	2.01
				IV	1.94							VI	1.92	VI	1.90	VI	1.95			VI	1.91
				IV	1.88					VI	1.84	VI	1.80			VI	1.83	VI	1.83	VI	1.85
																VI	1.74	VI	1.74	VI	1.74
				VI	1.75							VI	1.74								
V	1.73	V	1.73	VI	1.73							V	1.71	VI	1.73						
VI	1.66	VI	1.66	V	1.69									V	1.68					III	1.68
						V	1.67	V	1.67	V	1.66	VI	1.66			VI	1.66				
						VI	1.64	VI	1.64							IV	1.64	IV	1.64		
VI	1.61	VI	1.61	IV	1.61									VI	1.62	VI	1.60	V	1.60	VI	1.61
				VI	1.57							VI	1.58			VI	1.56				
III	1.53	III	1.53	V	1.54											V	1.52	VI	1.54	III	1.54
				V	1.50	III	1.48	III	1.48	IV	1.49	V	1.49	V	1.51	IV	1.50	III	1.50	VI	1.50
												V	1.46			VI	1.45			VI	1.47
				IV	1.43							VI	1.44	VI	1.43	VI	1.42	VI	1.42	VI	1.43
				VI	1.41							V	1.41								
				V	1.40															VI	1.40
										VI	1.38					VI	1.38				
				V	1.37							VI	1.36			V	1.36			V	1.36
				V	1.34											V	1.34	V	1.34		
				V	1.33							VI	1.32							V	1.33
V	1.31	V	1.31	V	1.30															V	1.31
														VI	1.30	V	1.29	V	1.29	VI	1.28
V	1.27	V	1.27	V	1.28	V	1.28	V	1.28	V	1.28			VI	1.28	VI	1.27	VI	1.27		
														VI	1.26	V	1.24	V	1.24	VI	1.25
				VI	1.23	V	1.23	V	1.23	V	1.23										
				VI	1.22											VI	1.22	VI	1.22	VI	1.22
				V	1.20							VI	1.21					VI	1.20		
						VI	1.19	VI	1.19									VI	1.18		
				V	1.18																
				V	1.17																
				VI	1.16																

NONTRONITE		NONTRONITE + GLYCEROL		CRISTOBALITE		HALLOYSITE		HALLOYSITE + GLYCEROL		INDIANAITE				ATTAPULGITE		MUSCOVITE		SERICITE		BIOTITE	
										Metahalloysite + Halloysite		Hydrargillite + Metahalloysite + Halloysite									
i	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*	*i*	*d*
VI	1.14	VI	1.14	VI	1.15	VI	1.15	VI	1.15									VI	1.15		
																		VI	1.12		
				VI	1.11													VI	1.11		
						VI	1.10	VI	1.10												
				V	1.09																
						VI	1.08	VI	1.08									VI	1.08		
VI	1.04	VI	1.04																		
						VI	1.02	VI	1.02												
VI	0.99	VI	0.99																		

FIXATION OF NITROGEN IN RICE SOILS BY ALGAE AS INFLUENCED BY CROP, CO_2, AND INORGANIC SUBSTANCES

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Received for publication November 3, 1949

The observation[2] that a considerable amount of nitrogen is fixed by algae when rice soils are waterlogged and exposed to sunlight has naturally raised the question whether similar fixation takes place also in presence of the crop. Under normal conditions, algae and rice plants grow together in the soil, and growth of the one may influence growth of the other. An association of two organisms growing in a common habitat and obtaining nutrients therefrom may have a beneficial effect on the growth of either, if one of them supplies the needs of the other. On the other hand, such an association may have a harmful effect, if the organisms compete for the supply of available nutrients or if one makes conditions otherwise unfavorable for growth of the other. To understand the role played by algae in the process of nitrogen recuperation in rice soils, it seemed desirable, therefore, to investigate the effect of the rice crop on the fixation of nitrogen by algae.

EXPERIMENTAL

Effect of crop on nitrogen fixation

Soil samples were taken, to a depth of 6 inches, from Faridpur, Bengal (pH 8.2), and from Sibsagar, Assam (pH 5.4). Fifteen-gram portions were waterlogged by addition of 100 ml. of distilled water in 250-ml. Erlenmeyer flasks. These were then divided into two sets, one of which was left uncropped, and the other cropped by placing a rice seedling in each, and holding it in position by loosely plugging the mouth of the flask with cotton wool. From a lot obtained from the Government Farm at Dacca, healthy-looking seedlings similar in size were selected. Their tops were cut, and several subsamples, each consisting of 20 seedlings, were then selected at random. One of these subsamples was used for transplantation, and two others were oven-dried, weighed, divided into 1-gm. portions, and analyzed for total nitrogen. The following results show that the samples were fairly uniform:

Dry weight of 20 seedlings, gm.	*Total nitrogen per gram dry material, mgm.*	*Average nitrogen per seedling, mgm.*
9.60	7.32	3.5
8.89	7.04	3.1

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[1] The work described in this paper was done before the senior author left Dacca University in September 1947.

The authors' thanks are due to D. L. Mukherjee, who carried out some of the preliminary experiments described in this paper, and also to the Indian Council of Agricultural Research for the financial assistance.

[2] De, P. K. The problem of nitrogen supply of rice: I. *Indian Jour. Agr. Sci.* 6: 1237–1245. 1936.

It was thought that the very small amounts of nutrients present in 15 gm. of soil in this experiment might be inadequate for growth of both the algae and the rice plant, and if algal growth failed or was inhibited, it would be difficult to say whether this was due to nutrient deficiency or to some effect of the plant. Consequently, a second experiment was performed simultaneously. In this, the soil was waterlogged by addition of 100 ml. of the following solution instead of water, thus providing additional nutrients for growth of algae: K_2HPO_4, 0.5 gm.; $MgSO_4 \cdot 7H_2O$, 0.2 gm.; $CaSO_4$, 0.1 gm.; $Ca_3(PO_4)_2$, 1.0 gm.; $FePO_4$, 0.1 gm.; $FeCl_3$ (1 per cent), 2 drops; distilled water, 1,000 ml.

In these first experiments which were run from mid-August to the end of December the flasks were exposed to sunlight[3] in the pot-culture house and were protected from rains, dust, and other contamination by a glass cover.

In Faridpur soil, algae appeared in a week with considerable evolution of gases. The growth gradually increased in bulk and eventually covered the entire soil surface. In some cases it even floated on top of the surface water. No difference in the amount of growth in different cultures was noticeable in the initial stages, but the cropped flasks later showed considerably heavier growth than the corresponding uncropped ones. The most luxuriant growth took place in the cropped flasks treated with nutrient solution. In these cultures the growth was so heavy that the flasks appeared to contain nothing but a green semisolid mass.

In Sibsagar soil, on the other hand, there was no visible algal growth in the control soil (soil + water) without crop. Even the flasks receiving nutrient solution showed no appreciable growth within a month, but thereafter a greenish film gradually appeared. As in the Faridpur soil, this ultimately made much heavier growth in the cropped flasks.

None of the rice plants looked healthy. There was no noticeable increase in the size of the seedlings, and the number of leaves remained about the same as at the start. Nevertheless, the plants remained alive until the end and formed an extensive root system in the soil.

At the conclusion of the experiment, several flasks were selected from each treatment for the determination of total nitrogen. For this purpose the entire contents of the culture vessel, including the rice plant if present, were transferred to a Kjeldahl flask, any residue adhering to the sides of the vessel being washed out with pure concentrated H_2SO_4. The liquid was boiled until the organic matter began to char; 5 gm. of anhydrous K_2SO_4 and a crystal of $CuSO_4$ were then added to the flask and digestion was carried out in the usual way, heating being continued for 1 hour after the liquid had become colorless. Ammonia formed was distilled under 0.1 N H_2SO_4 and estimated by back titration, methyl red being used as indicator. The results are given in table 1.

The results show that in presence of the crop the fixation of nitrogen was considerably increased. This is true for both the control (soil + water) and the treated soils (soil + solution). In the treated soils the fixation was greater than in the corresponding control soils. This shows that algal growth was stimulated by the nutrients added.

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[3] As the cultures were sometimes overheated by the intense sunlight, the flasks in all subsequent experiments were placed in a large shallow bath of running water. Under these conditions, algae remained healthy, fixation of nitrogen was much greater, and agreement among the replicate results was closer.

In view of these results, the experiments were repeated the following winter on the Faridpur and Sibsagar soils and on a soil from Coimbatore. The results (table 2) are in general agreement with the previous ones, although in the winter experiments much less nitrogen was fixed, presumably because of low temperature and shorter exposure to sunlight. The fact that much more nitrogen is fixed in presence of the crop is definitely indicated by both sets of experiments.

TABLE 1

Effect of crop on nitrogen fixation in rice soils from mid-August to the end of December

TREATMENT	NITROGEN PER CULTURE FLASK		
	At start	At end	Fixed
	mgm.	*mgm.*	*mgm.*
Faridpur soil			
Soil + water	7.7	13.5	5.8
		13.4	5.7
		14.5	6.8
			Av. 6.1
Soil + water + plant	11.0	20.2	9.2
		21.0	10.0
		21.6	10.6
			Av. 9.9
Soil + solution	7.7	18.0	10.3
		15.4	7.7
		17.0	9.3
			Av. 9.1
Soil + solution + plant	11.0	31.8	20.8
		33.8	22.8
		31.1	20.1
		29.4	18.4
			Av. 20.7
Sibsagar soil			
Soil + solution	20.3	26.8	6.5
		26.1	5.8
		27.5	7.2
			Av. 6.5
Soil + solution + plant	23.6	36.8	13.2
		36.6	13.0
		37.0	13.4
			Av. 13.2

It is interesting that nitrogen was fixed in Sibsagar soil only in presence of the crop or of nutrient solution. Previous experiments with soils having pH values below 6 showed little or no fixation of nitrogen, from which it was concluded

TABLE 2

Effect of crop on nitrogen fixation in rice soils during January and February

TREATMENT	NITROGEN PER CULTURE FLASK		
	At start	At end	Fixed
	mgm.	*mgm.*	*mgm.*
Faridpur soil			
Soil + water	7.1	8.3	1.2
		9.4	2.3
		9.8	2.7
		9.9	2.8
			Av. 2.3
Soil + water + plant	10.1	15.1	5.0
		13.7	3.6
		14.3	4.2
			Av. 4.3
Soil + solution	7.1	11.2	4.1
		11.0	3.9
		12.6	5.5
			Av. 4.5
Soil + solution + plant	10.1	20.0	9.9
		20.9	10.8
		21.4	11.3
			Av. 10.6
Coimbatore soil			
Soil + water	11.1	15.1	4.0
		13.4	2.3
		13.7	2.6
		13.8	2.7
			Av. 2.9
Soil + water + plant	14.1	20.7	6.6
		20.0	5.9
		19.5	5.4
			Av. 6.0
Soil + solution	11.1	12.6	1.5
		14.1	3.0
		13.7	2.6
			Av. 2.4
Soil + solution + plant	14.1	22.7	8.6
		33.6	19.5*
		25.8	11.7
			Av. 13.3

TABLE 2—*Continued*

TREATMENT	NITROGEN PER CULTURE FLASK		
	At start	At end	Fixed
	mgm	*mgm.*	mgm
Sibsagar soil			
Soil + water	20.3	No algal growth	
Soil + water + plant	22.3	23.6	1.3
		25.5	3.2
		24.8	2.5
			Av. 2.3
Soil + solution	20.3	21.8	1.5
		21.3	1.0
		22.4	2.1
			Av. 1.5
Soil + solution + plant	22.3	31.8	9.5
		32.2	9.9
		31.5	9.2
			Av. 9.5

* Growth was abnormally heavy in comparison with that in parallel flasks.

that the algae responsible for fixation were unable to grow under conditions of such acidity. This conclusion received further support from the fact that nitrogen fixation took place in those soils when they were treated with $CaCO_3$. The observation with Sibsagar soil now shows that even in acid soils fixation takes place if a crop is present. This was confirmed by examining a few more soils of pH below 6.

Effect of condition of crop growth on nitrogen fixation

An experiment was next performed to determine whether difference in growth of the rice plants had any effect on the fixation of nitrogen. Fifteen-gram portions of the Faridpur and Coimbatore soils were waterlogged as before by addition of either water or nutrient solution. The cultures were then divided into three sets, each planted with seedlings of different age and consequently of different size. The transplanted seedlings failed to make healthy growth in any of the cultures, which was not unexpected in view of the small amount of soil. Nevertheless, there were appreciable differences in growth of the seedlings of different ages: the older seedlings remained healthier throughout than the younger ones. The results, given in table 3, show that the fixation of nitrogen increased with the age of the seedlings. It thus appears that the vigor of the plant growth has some influence on fixation of nitrogen in rice soils by algae: the healthier the growth, the greater is the fixation.

Nature of effect of crop on nitrogen fixation

The increased fixation of nitrogen in presence of the crop may be due to: (*a*) Decomposition of the dead roots, which by serving as energy materials stimulated growth and activity of the nitrogen-fixing organisms. (*b*) Absorption by the plant of toxic metabolic products of the algae, thus making conditions continually favorable for growth of the latter. There is also the possibility that the plants have secreted some growth-promoting substances having a beneficial effect on growth of the algae. (*c*) The greater supply of CO_2 in the cropped soil as a result of the respiration of the plant, making conditions more favorable for photosynthesis by the algae. In this connection it is noteworthy that Allison and Morris[4] observed much greater fixation of nitrogen by a pure culture of an *Anabaena* when air containing 1 per cent CO_2 was bubbled through the solution.

These hypotheses were tested by the following experiments.

Effect of decomposition of rice roots. Fifteen-gram portions of the Faridpur soil and of a soil from Sabour were waterlogged as in the previous experiments and were treated with 1 gm. of rice roots. The roots, taken from some seedlings about 2 months old, were thoroughly washed to remove adhering soil particles, then cut off with scissors and chopped into small pieces. Since oven-drying might bring about changes in composition of the material, which might affect its decomposability, the chopped roots were dried between blotting papers, and the materials thus obtained were quickly weighed and introduced into different cultures. The cultures were then exposed to sunlight for about 3 months. The algal growth that appeared was pale yellow and looked very unhealthy; the ultimate growth was much less than in the cropped cultures. Table 4 gives the results of nitrogen determinations.

Since this experiment was performed simultaneously with one on the effect of CO_2 on nitrogen fixation (table 6), it is permissible to use some of the data of the latter experiment for interpretation of the present results. Figures in columns 2 and 4 in table 4 were accordingly taken from table 6.

The addition of rice roots undoubtedly brought about an increase in the fixation of nitrogen, but this was far less than that brought about in presence of the crop. It appears, therefore, that the effect of the crop is not due, to any large degree, to decomposition of the roots. Furthermore, as the weight of root added to each culture is obviously far greater than can be contributed by an unhealthly plant, such as one obtained in this experiment, the importance of root decomposition in this process becomes almost insignificant.

Absorption of metabolic products. The validity of this hypothesis was tested by an indirect method, namely, by observing the effect of addition of the growth-promoting substances and of removal of the toxic products on the fixation of nitrogen in an uncropped soil. It was thought that under these conditions an uncropped soil, having the supposed advantages of growing plants, would behave like a cropped soil and consequently would show considerable increase in fixation of nitrogen. The experiment consisted in setting up two cultures—one cropped and the other uncropped—in such a way that the supernatant liquid of the one could easily be transferred to the other and then returned to

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[4] Allison, F. E., and Morris, H. J. Nitrogen fixation by blue-green algae. *Proc. 2nd Internatl. Cong. Soil Sci. Comn.* 3: 24–28. 1932.

TABLE 3

Effect of condition of crop growth on fixation of nitrogen

AGE OF SEEDLING	TREATMENT	NITROGEN PER CULTURE FLASK		
		At start*	At end	Fixed
weeks		*mgm.*	*mgm.*	*mgm.*
		Faridpur soil		
2	Soil + water	8.2	14.7	6.5
		8.2	15.0	6.8
		8.2	15.1	6.9
				Av. 6.7
	Soil + solution	8.2	17.8	9.6
		8.2	17.5	9.3
		8.2	18.1	9.9
				Av. 9.6
4	Soil + water	8.8	16.0	7.2
		8.8	16.4	7.4
		8.8	15.8	7.0
		8.8	16.2	7.4
				Av. 7.3
	Soil + solution	8.8	19.5	10.7
		8.8	19.0	10.2
		8.8	20.3	11.5
		8.8	20.6	11.8
				Av. 11.1
6	Soil + water	9.4	17.8	8.4
		9.4	18.1	8.7
		9.4	19.5	10.1
		9.4	17.8	8.4
				Av. 8.9
	Soil + solution	9.4	22.6	13.2
		9.4	23.5	14.1
		9.4	24.4	15.0
		9.4	22.0	12.6
				Av. 13.7
		Coimbatore soil		
2	Soil + water	12.2	21.2	9.0
		12.2	20.6	8.4
		12.2	20.3	8.1
				Av. 8.5
	Soil + solution	12.2	24.8	12.6
		12.2	23.1	10.9
		12.2	24.1	11.9
				Av. 11.8

TABLE 3—*Continued*

AGE OF SEEDLING	TREATMENT	NITROGEN PER CULTURE FLASK		
		At start*	At end	Fixed
weeks		*mgm.*	*mgm.*	*mgm.*
		Coimbatore soil—Continued		
4	Soil + water	12.8	22.6	9.8
		12.8	22.3	9.5
		12.8	23.4	10.6
		12.8	23.4	10.6
				Av. 10.1
	Soil + solution	12.8	26.8	14.0
		12.8	25.9	13.1
		12.8	26.5	13.7
		12.8	26.2	13.4
				Av. 13.6
6	Soil + water	13.4	25.5	12.1
		13.4	25.4	12.0
		13.4	24.8	11.4
		13.4	25.9	12.5
				Av. 12.0
	Soil + solution	13.4	30.4	17.0
		13.4	28.7	15.3
		13.4	31.1	17.7
		13.4	30.4	17.0
				Av. 16.8

* In 15 gm. Faridpur soil, 7.4 mgm. +N in one seedling; in 15 gm. Coimbatore soil, 11.4 mgm. +N in one seedling.

the original, the idea being that by this process the soluble products formed in each would be distributed between the two. Thus, any growth-promoting substances formed in the cropped cultures would pass on to the uncropped cultures and any toxic products formed in the latter would pass on to the former to be absorbed there by the plants. In either case the conditions would become favorable for the fixation of nitrogen in the uncropped culture. The experiment was carried out on the Faridpur and Coimbatore soils as follows:

The experimental unit was a 250-ml. pyrex Erlenmeyer flask to which was fused, about 1 inch from the bottom, a horizontal side tube about 7 mm. in diameter. Two such flasks were joined in a series by connecting the side tubes with rubber tubing. The connecting tube was closed with a screw clamp, and a 15-gm. portion of soil was placed in each flask. The soil in both flasks was then waterlogged by addition of 200 ml. of distilled water or of solution. The whole set of flasks was then placed in a bath of running water and exposed to sun. After the soil had settled and the supernatant water had become clear, one of the flasks in each series was planted with a rice seedling. The screw clamp was then opened to allow contact between the liquids in the two flasks. At frequent intervals, the flasks in each series were slowly raised, one after the other, to mix the supernatant liquids. The experiment was continued for 2½ months, after which the total nitrogen content of each flask was determined. For comparison, control cultures with soil plus water or solution, without crop and not arranged in series, were maintained simultaneously. The results are given in table 5.

TABLE 4

Effect of decomposition of rice roots on fixation of nitrogen

TREATMENT	NITROGEN FIXED PER CULTURE FLASK		
	Uncropped	Uncropped + roots	Cropped
	mgm.	*mgm.*	*mgm.*
Faridpur soil			
Soil + water	2.7	5.8	8.3
	1.9	4.1	9.0
	1.4	6.1	11.1
	1.0	4.4	9.7
Av.	1.8	5.1	9.5
Soil + solution	4.3	8.0	38.4
	3.8	8.9	38.6
	4.5	7.2	35.5
	3.6	7.5	40.1
Av.	4.1	7.9	38.2
Sabour soil			
Soil + water	3.4	6.9	11.4
	3.2	6.8	14.9
	2.9	6.3	14.2
	2.7	6.5	13.1
Av.	3.1	6.6	13.4
Soil + solution	4.5	10.1	29.3
	5.6	8.2	28.2
	5.0	10.4	25.7
	5.2	—	27.2
Av.	5.1	9.6	27.6

The fixation of nitrogen in the uncropped flasks in series with the cropped ones was only slightly greater than that in the control (not in series) and considerably less than that in the cropped flasks. This shows that the growing rice plant had no beneficial effect on the fixation of nitrogen in the uncropped

TABLE 5

Influence of transfer of supernatant liquid from a cropped to an uncropped soil and vice versa on fixation of nitrogen by algae

TREATMENT	NITROGEN PER CULTURE FLASK		
	At start	At end	Fixed
	mgm.	*mgm.*	*mgm.*
Faridpur soil			
Soil + water	7.4	10.5	3.1
		11.0	3.6
		10.8	3.4
			Av. 3.4
In series			
Soil + water	7.4	12.0	4.6
		11.2	3.8
		11.5	4.1
			Av. 4.2
Soil + water + plant	12.2	22.2	10.0
		22.7	10.5
		22.8	10.6
			Av. 10.4
Soil + solution	7.4	11.7	4.3
		12.0	4.6
		11.7	4.3
			Av. 4.4
In series			
Soil + solution	7.4	12.6	5.2
		12.3	4.9
		13.7	6.3
			Av. 5.5
Soil + solution + plant	12.2	36.2	24.0
		33.8	21.6
		35.6	23.4
			Av. 23.0
Coimbatore soil			
Soil + water	11.4	16.1	4.7
		14.4	3.0
		15.1	3.7
			Av. 3.8
In series			
Soil + water	11.4	16.5	5.1
		17.2	5.8
			Av. 5.5

TABLE 5—*Continued*

TREATMENT	NITROGEN PER CULTURE FLASK		
	At start	At end	Fixed
	mgm.	*mgm.*	*mgm.*
Soil + water + plant	16.2	31.6	15.4
		34.8	18.6
			Av. 17.0
Soil + solution	11.4	15.2	3.8
		16.1	4.7
		15.8	4.4
			Av. 4.3
In series			
Soil + solution	11.4	17.9	6.5
		18.9	7.5
			Av. 7.0
Soil + solution + plant	16.2	40.7	24.5
		43.9	27.7
			Av. 26.1

flasks in series, although the supernatant liquids of the cultures were in contact. The results thus lend no support to the present hypothesis.

Effect of CO_2 supply. The following experiment was performed on the Faridpur and Sabour soils to study the effect of CO_2 supply on the fixation of nitrogen by algae:

A set of nine Erlenmeyer flasks, each containing 15 gm. of soil and 100 ml. of distilled water or solution and closed with a rubber stopper carrying two glass tubes bent at right angles, were connected in series by means of rubber tubing. Four of the flasks contained soil plus water, four soil plus solution, and the remaining one only distilled water. In each set a flask with soil plus water was alternated with one with soil plus solution, the middle position being occupied by the flask containing distilled water. For each soil two such sets were made: one was aerated with air, and the other with air containing 2 per cent CO_2, the gases being passed over the water surface. The different sets were placed in a shallow water bath and exposed to sun. One of the two end tubes of each set was then connected to an aspirator bottle containing the gas mixture, the other tube serving as an outlet. Except for 2 weeks after the start when no gas mixture was passed, the flasks were aerated twice daily, in early morning and at noon, with 4 liters of gas mixture each time. The two sets for each soil were aerated simultaneously, the rate of flow of gas being equal in both cases. For comparison, cropped cultures were also set up simultaneously (not aerated). The flasks containing water were periodically taken out for determination of pH; it was found that in the CO_2 series the pH of the water never fell below 5.8. Total nitrogen was determined after 3 months, and the results obtained (table 6) were compared with the fixation observed in presence of the crop.

In every instance more nitrogen was fixed in the cultures aerated with CO_2 than in the corresponding ones with air. This shows that algal growth is stimulated by increasing the supply of CO_2 in the surrounding air. In the soil-solution mixture aerated with CO_2, nitrogen fixation was considerable, being nearly as much as in the corresponding cropped cultures. This suggests that the plant supplies CO_2 to algae. But when the results obtained with soil-water mixture are compared with those of the corresponding cropped cultures, it is found that more nitrogen was fixed in presence of the crop. In this case, therefore, CO_2

TABLE 6

Effect of CO_2 supply on the fixation of nitrogen in rice soils

TREATMENT	NITROGEN FIXED PER CULTURE FLASK		
	Uncropped		
	Aerated with air	Aerated with CO_2	Cropped
	mgm.	*mgm.*	*mgm.*
Faridpur soil			
Soil + water	2.7	4.8	8.3
	1.9	4.9	9.0
	1.4	5.7	11.1
	1.0	4.1	9.7
Av.	1.8	4.9	9.5
Soil + solution	4.3	32.1	38.4
	3.8	35.7	38.6
	4.5	31.1	35.5
	3.6	31.4	40.1
Av.	4.1	32.6	38.2
Sabour soil			
Soil + water	3.4	6.2	11.4
	3.2	8.3	14.9
	2.9	5.5	14.2
	2.7	6.4	13.1
Av.	3.1	6.6	13.4
Soil + solution	4.5	30.0	29.3
	5.6	29.8	28.2
	5.0	31.8	25.7
	5.2	—	27.2
Av.	5.1	30.4	27.6

appears to be less effective than the plant in stimulating algal growth. This difference in the behavior of soil-solution and soil-water mixtures, with regard to the effect of CO_2, is probably explained by assuming that plants benefit algal growth in two ways: first, by supplying CO_2, and second, by dissolving certain mineral constituents of soil and rendering them available to algae. When nutrients are present in sufficient amounts, as in the soil-solution mixtures, this second effect of the plant is not evident, since the algae already have enough mineral nutrients to satisfy their needs. In this case, the beneficial effect of the plant lies almost entirely in supplying CO_2 to the algae. This is why nitrogen fixation is almost the same in soil-solution mixtures aerated with CO_2 as in the corresponding cropped culture. In the soil-water mixture, on the other hand, the algal growths in presence of the crop have the double advantage of obtaining both CO_2 and a part of the minerals made available, whereas those in absence of the plant obtain CO_2 but no minerals. This probably explains why in this case there is more fixation of nitrogen in presence of the crop.

At anyrate, the results clearly show that nitrogen fixation in the uncropped soil is stimulated by increasing the supply of CO_2 in the soil atmosphere. From these observations it is reasonable to conclude that the stimulating effect of the plant is largely due to the increased supply of CO_2.

Effect of inorganic substances on nitrogen fixation

In a previous experiment (tables 1 and 2) it was observed that growth and fixation of nitrogen by algae were considerably stimulated by addition of a nonnitrogenous inorganic mixture. Whether this was due to the combined effect of all the constituents of the mixture or to one or two particular constituents, however, was not ascertained. To investigate this point, an experiment was carried out in which the Sibsagar, Faridpur, and Sabour soils and a soil from Karimgunj were treated with different inorganic substances, added singly or in combination, and the effect of such treatments on the fixation of nitrogen was determined. The experimental procedure was the same as that previously described.

The results (table 7) show that nitrogen fixation was considerably stimulated by addition of calcium phosphate although not to the same degree as by complete solution. Potassium sulfate, on the other hand, showed a depressing effect when added alone, but when it was used in combination with calcium phosphate this effect was not noticeable.

Very similar results were also obtained in a second experiment in which phosphate, calcium phosphate, and magnesium sulfate were used in different combinations. Magnesium sulfate, like potassium sulfate, showed a depressing effect when added alone, but not when used in combination with either potassium or calcium phosphate. Like calcium phosphate, potassium phosphate stimulated nitrogen fixation, but here again the fixation was less than in the complete solution. A combination of two phosphates (Ca + K) was tried, but the fixation was not greater than with either added alone.

The results, on the whole, show that fixation of nitrogen by algae is stimulated by phosphates whether added in soluble form as potassium phosphate or in insoluble form as calcium phosphate. It appears, therefore, that the stimulating effect of the complete solution is due mainly, though not entirely, to phosphates. Although the fixation is less with phosphate alone than with complete solution, the former is advantageous from a practical point of view in that only one substance is used instead of a mixture of several. The observation that calcium phosphate stimulates nitrogen fixation by algae has a practical bearing and suggests that application of bone meal or superphosphate to rice soil would enrich the soil not only with phosphorus but also with nitrogen.

TABLE 7

Effect of addition of some nonnitrogenous inorganic substances on fixation of nitrogen by algae

TREATMENT*	NITROGEN PER CULTURE FLASK			
	At start†	At end‡	Fixed	Increase, as per cent of total in soil
	mgm.	*mgm.*	*mgm.*	
Sibsagar soil				
1. Soil + water + plant	25.0	34.8	9.8	50.8
2. Treatment 1 + Ca	25.0	39.2	14.2	73.6
3. Treatment 1 + K	25.0	31.9	6.9	35.8
4. Treatment 1 + Ca + K	25.0	40.4	15.4	79.8
5. Soil + solution + plant	25.0	45.7	20.7	107.3
Faridpur soil				
1. Soil + water + plant	14.4	25.1	10.7	123.0
2. Treatment 1 + Ca	14.4	30.7	16.3	187.4
3. Treatment 1 + K	14.4	22.3	7.9	90.8
4. Treatment 1 + Ca + K	14.4	31.1	16.7	193.2
5. Soil + solution + plant	14.4	44.7	30.3	348.2
Karimgunj soil				
1. Soil + water + plant	19.3	29.4	10.1	74.3
2. Treatment 1 + Ca	19.3	36.6	17.3	127.2
3. Treatment 1 + K	19.3	27.5	8.2	60.3
4. Treatment 1 + Ca + K	19.3	38.3	19.0	139.7
5. Soil + solution + plant	19.3	43.8	24.5	180.2
Sabour soil				
1. Soil + water + plant	24.3	38.4	14.1	86.5
2. Treatment 1 + Ca	24.3	41.8	17.5	109.8
3. Treatment 1 + K	24.3	32.6	8.3	50.9
4. Treatment 1 + Ca + K	24.3	42.4	18.1	111.0
5. Soil + solution + plant	24.3	44.8	20.5	125.8

* Ca = 0.1 gm. $Ca_3(PO_4)_2$ per flask; K = 0.05 gm. K_2SO_4 per flask.

† In 15 gm. Sibsagar soil 19.3 mgm. + 5.7 mgm. in one seedling; in 15 gm. Faridpur soil 8.7 mgm. + 5.7 mgm. in one seedling; in 15 gm. Karimgunj soil 13.6 mgm. + 5.7 mgm. in one seedling; in 15 gm. Sabour soil 16.3 mgm. + 8 mgm. in one seedling.

‡ Figures are averages of four replicates.

SUMMARY

Both growth and fixation of nitrogen by algae in rice soils are considerably increased in presence of the crop. This increase is much greater if the soil is treated with a nonnitrogenous inorganic mixture.

Even soils having pH values of less than 6, in which no nitrogen is fixed in the uncropped condition, show appreciable fixation when the crop is present. The fixation in presence of the crop appears to depend on the condition of the plants: the healthier the growth, the greater is the fixation.

Decomposition of rice roots in soils results in some fixation of nitrogen, but the amount thus fixed is small in comparison with the fixation in presence of the crop. This shows that the stimulating effect of the crop is not due to root decomposition.

There is no evidence either of secretion by the plant of growth-promoting substances capable of stimulating algal growth, or of absorption by the plant of toxic metabolic products of algae.

Fixation of nitrogen by algae in absence of the crop is considerably stimulated by passing air containing 2 per cent CO_2 over the surface water. It is concluded that the stimulating effect of the crop is largely due to increased supply of CO_2 evolved as a result of respiration and root decomposition.

Addition of phosphates to rice soil, whether in soluble form as potassium phosphate or in insoluble form as calcium phosphate, stimulates the fixation of nitrogen by algae. On the other hand, potassium or magnesium sulfate, when applied singly, has a depressing effect, but this effect is not noticeable when the two are used in combination with phosphates.

COMPARATIVE FLUORINE UPTAKE BY PLANTS IN LIMED AND UNLIMED SOIL

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Received for publication June 6, 1949

The investigations reported herein were undertaken to determine the extent to which fluorine can be absorbed from soils by plant roots, and the extent to which the absorption can be controlled by liming. Sassafras loamy sand, having a pH value near 5.0 and containing 12 ppm. of naturally occurring fluorine, was transported from near Springtown Corners, N. J., to a greenhouse of the Division of Cereal Crops and Diseases at Beltsville, Md., where the experiments were carried out.

METHODS

Crop 1

The soil was placed in a greenhouse bench that was divided by wooden partitions into compartments, into each of which was weighed enough soil to give 200 pounds, oven-dry basis. Half of the plots were limed to near pH 7.5 by incorporation of 90 gm. of slaked lime, corresponding roughly to a ton per acre, and thoroughly mixed. The soil was kept damp for a week, during which it was remixed several times before the other materials were added.

The soil was suspected of being deficient in nutrients, but because calcium could not be added without precipitating fluorine, a calcium-containing fertilizer could not be added. Twenty-five grams of ammonium nitrate solution was mixed into the soil of each plot 6 days after it was limed. Later, 6.4 gm. of potassium phosphate and 5 gm. of potassium sulfate were added to each plot, in solutions that were poured into trenches between the rows of plants.

A week after the nitrate additions, sodium fluoride in solution and hydrofluoric acid, greatly diluted, were mixed thoroughly into some of the plots, limed and unlimed, in such quantity as to supply 15 ppm. of fluorine, based on the oven-dry weight of the soil. Collard seeds were sown 2 days later, April 12, 1946.

From a preliminary experiment with pot cultures it was determined that as little as 50 ppm. of fluorine as NaF was toxic to collards in this soil. To attain a barely toxic concentration in the plots, it was planned to build up the fluorine gradually to this concentration, from the initial application before sowing, by frequent additions of solutions that contained the desired aliquots of HF and

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[1] Fluorine analyses were made by Hy Almond and Ewel Dodson under the supervision of W. O. Robinson, senior chemist of the Division of Soils, Fertilizers, and Irrigation. The writer is also indebted to S. W. Griffin, chemist, Division of Cereal Crops and Diseases, for helpful suggestions, and for the standardized hydrofluoric acid solutions used in the investigation.

NaF. The rows of plants were 6 inches apart, and the solutions were poured into shallow trenches between the rows. Great care was exercised to prevent dropping or spattering the solutions on the leaves.

The first application was made when the plants were 6 days old. Twenty-two such applications, each supplying 1 ppm. of fluorine, were made during the first 5 weeks. Concentration of the stock solution then was increased, so that the aliquots supplied 2 ppm. of fluorine, and then 3 ppm., to hasten the full addition of 50 ppm., which was attained June 3, approximately 6 weeks after the first application.

Calcium fluoride also was added to a limed and an unlimed plot for comparison with the more soluble fluorides. Because of its relative insolubility, the entire amount of CaF_2 required for an addition of 50 ppm. of fluorine (9.32 gm. in 200 pounds of dry soil) was mixed into the soil 2 days before the seed was planted.

The plants were cut on June 7, at the age of 2 months, dried in an unheated oven with forced ventilation, and ground for analysis.

It should be noted that the method of supplying fluorides to the plants, as solutions poured between the rows, does not establish the exact concentration in contact with the roots at any given time. The applications, however, were always followed by watering, which, in view of the very sandy type of soil, is believed to have kept the fluorides distributed fairly evenly. To preclude leaching, the water added was limited by measurement.

Crop 2

The soil lots were turned and mixed thoroughly, and a second crop of collards was sown 4 days after the first was cut. No more fluorine was added to the plots that had received CaF_2 but to the others, the additions of HF and NaF were resumed, when the plants had reached a height of several inches, at a rate of 2 ppm. of fluorine per application. On July 1, a mineral salt solution was poured into the trenches between the rows, in such quantity as to supply 5 gm. each of potassium sulfate, potassium phosphate, and ammonium nitrate.

Marked stunting of the plants in two of the fluorine-treated plots made it seem advisable to stop the fluorine applications after 2 weeks, when the plots had received a total of 78 ppm. of fluorine. The plants were cut on July 25, at the age of 6 weeks, dried in a ventilated oven that was maintained at a constant temperature of 90°F., and ground for analysis.

Crop 3

Again the soil in each compartment was turned and thoroughly mixed, and buckwheat was sown on July 26. Applications of the hydrogen and sodium fluorides were resumed after the plants had reached a height of several inches, and were continued at a rate of 2 ppm. of fluorine daily until August 16, when the soil had received a total addition of 102 ppm. The applications were then discontinued because of injury to some of the plants. On August 30, the plants were cut and dried in the ventilated oven at 90°F., and ground for analysis.

Throughout the experiment, water was poured between the rows of plants in the check plots in the same volumes and at the same times as the fluoride solutions that were applied to the fluorinated plots.

RESULTS

Analyses of fluorine in the plants from the various plots are given in table 1. The data show that plants in the unlimed plots always took up more fluorine than did those in the corresponding limed plots.

The greatest fluorine uptake occurred from that supplied as HF, and the least from that supplied as CaF_2. The lesser uptake of the fluorine of NaF as compared with that of the acid may be due to the fact that NaF decreased the soil acidity somewhat (table 1). Scharrer and Schropp[2] reported that fluorine was more toxic in acid soil than in neutral soil.

TABLE 1

Fluorine contents and average dry weights of plants grown on limed and unlimed greenhouse plots treated with fluorides[1]

PLOT NO.	SOIL TREATMENT	FLUORINE CONTENT OF PLANTS (DRY TISSUES)			AVERAGE DRY WEIGHTS OF PLANTS			pH VALUES OF SOIL			
		Crop 1-Collards (50 ppm F added to soil)	Crop 2-Collards (78 ppm. F added to soil)	Crop 3-Buckwheat (102 ppm. F added to soil)	Crop 1-Collards (50 ppm F added to soil)	Crop 2-Collards (78 ppm F added to soil)	Crop 3-Buckwheat (102 ppm. F added to soil)	Before Cropping	After Crop 1	After Crop 2	After Crop 3
		ppm	*ppm.*	*ppm.*	*gm.*	*gm.*	*gm.*				
1	HF	96.0†	262†	9900‡	.25†	.19†	.10‡	4.9	5.0	5.0	4.5
1a	HF plus lime	13.0	30.7	900	.76	.69	.47	7.5	6.4	6.6	6.2
2	NaF	68.0	111†	2450‡	.46	.26†	.27‡	5.0	5.8	5.7	5.2
2a	NaF plus lime	45.0	18.2	87	.80	.69	.42	7.4	6.7	6.7	7.0
4	CaF_2	37.0	20.6§	—	.51	.45§	—	5.0	5.2	4.8	—
4a	CaF_2 plus lime	5.0	5.2§	—	.86	.74§	—	7.6	6.7	6.8	—
3	Check, unlimed	3.7	4.0	59	.45	.45	.36	4.8	4.8	4.7	4.5
3a	Check plus lime	3.2	3.0	10	.87	.73	.44	7.5	6.6	6.6	6.9

[1] The soil contained 12 ppm. of naturally occurring fluorine.

† Plants severely stunted, but leaves not injured.

‡ Plants severely stunted and leaves injured.

§ Figures are not comparable with others in the column because the soil was given only the initial application of 50 ppm. of fluorine.

In the unlimed plots, the quantities of fluorine taken up by the second collard crop from the soluble fluorides, HF and NaF, were greater than those found in the first harvest, as would be expected from the continuing applications of the fluoride during growth of this second crop. But plants from the corresponding limed plots contained less fluorine than had those of the first croppings. A possible explanation is that calcium from the added lime had become progressively more available, with consequent continuing precipitation of the fluorine as the relatively unavailable CaF_2.

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[2] Scharrer, K., and Schropp, W. Die Wirkung des Fluor-Ions auf Keimung und Jugendwachstum einiger Kulturpflanzen. *Landw. Vers. Sta.* 114: 203–214, 1932.

Of interest were the high fluorine contents of the buckwheat plants of the third crop, as well as the very great decrease in their fluorine uptake brought about by liming the soil.

Under natural conditions plants have not been found to contain much fluorine, even when grown on soils rather rich in it. None of the plants analyzed by Robinson[3] or other investigators to whom he refers had fluorine contents as high as did the buckwheat of table 1. The latter took up 59 ppm., more than any plant in Robinson's table, on the untreated check plot where the soil contained only 12 ppm. of naturally occurring fluorine.

The average dry weights of the plants (table 1) show their vigor of growth in relation to their fluorine contents. Plants of the first crop of collards that received a total of 50 ppm. of fluorine were injured only where hydrofluoric acid was added to unlimed soil. Consistently, these plants had the highest fluorine content. They were stunted but had no distinctive leaf symptoms (fig. 1). In the corresponding limed plot the plants were virtually uninjured, illustrating the fact shown by the work of MacIntire *et al.*[4] that calcium, by precipitating fluorine as the relatively insoluble CaF_2, so reduces availability of the fluorine to plants as to eliminate toxicity.

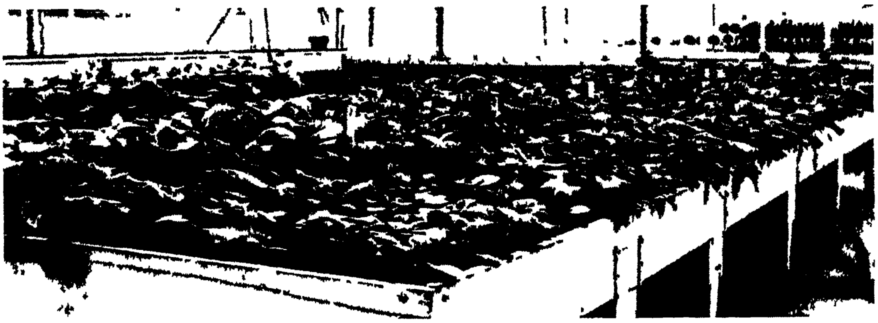

FIG. 1. COLLARDS OF FIRST CROP GROWING IN SOIL PLOTS IN GREENHOUSE BENCH

Plants nearest camera (plot 1) were stunted by 50 ppm. of fluorine added as hydrofluoric acid to unlimed loamy sand The adjacent much larger plants of the left (plot 1 a) were in limed soil given the same quantity of fluorine.

At the time of harvesting the second crop of collards, the plants of both unlimed plots receiving soluble fluorides, HF and NaF, were severely stunted, in accordance with their relatively high fluorine contents of 262 and 111 ppm., respectively. In the corresponding limed plots where the analyses show that fluorine uptake was low, the dry weights of the plants show no significant reduction below those of plants from the check plots.

Buckwheat plants of the third crop were also much stunted on the unlimed plots that had received HF and NaF. Leaf injury, consisting of marginal withering and chlorosis followed by necrosis and usually some spotting, was extreme on all plants in the unlimed plots that had received HF and was occasional in the plots that had received NaF (fig. 2). Neither fluoride injured the plants of the adjacent limed plots.

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[3] Robinson, W. O., and Edgington, G. Fluorine in soils. *Soil Sci.* 61: 341–353, 1946.

[4] MacIntire, W. H., *et al.* Fluorine content of plants fertilized with phosphates and slags carrying fluorides. *Indus. and Engin. Chem.* 34: 1469–1479, 1942.

The single application of CaF_2 that was stirred into the soil before the seeding of the first crop was not injurious to any crop on either the limed or the unlimed plot.

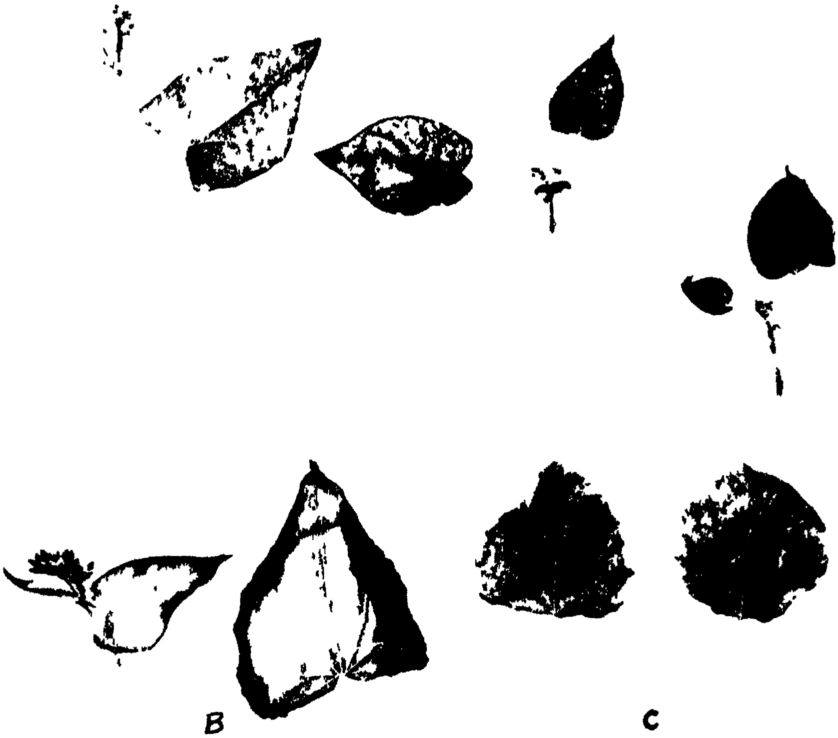

Fig. 2. Leaves of Buckwheat Plants Injured by Fluorides Added to an Unlimed Loamy Sand

A, Yellowish discoloration and marginal necrosis of leaves from plants grown in soil treated with 102 ppm. F as HF. Normal plant from untreated soil to the left; *B*, Early stage of marginal injury from a similar application of NaF; *C*, Later stage, showing necrosis of affected leaf margins.

That buckwheat is more tolerant of fluorine in its tissues than is the collard plant is evidenced in table 1. The collards were stunted wherever subsequent analysis showed them to contain 96 or more ppm. of fluorine. In contrast, buckwheat in the limed HF plot took up 900 ppm. without apparent injury. The data indicate that buckwheat absorbs fluorine more readily than do collards, and, from the evidence of this single comparison, is more tolerant of high concentrations in its tissues.

The pH values obtained for the plots before sowing and after harvesting each of the three crops are also summarized in table 1. The determinations were made with a glass electrode (Beckman pH meter) in soil samples moistened to a soft paste. Applications of HF had no appreciable effect on the acidity of the soil; NaF decreased it somewhat.

A test was made of the relative availability of the fluorine of fluorides added to the loamy sand from New Jersey and that added to a sandy loam, higher in colloidal material, of Beltsville, Md. These soils differed greatly in their original fluorine content, the former containing 12 ppm. and the latter 214 ppm. This difference is in accordance with Robinson's[3] statement that, in general, sandy soils are low, and heavier-textured soils high, in fluorine. The fluorine of the Beltsville soil, however, is evidently not readily available to plants, since it causes no symptoms of injury, whereas in the loamy sand, plants were stunted severely by applications of but 50 ppm. fluorine as HF (table 1).

TABLE 2

Comparative fluorine uptake by collard plants grown with sodium fluoride added to a loamy sand (A) and a sandy loam (B)†*

PLOT NO.	SOIL	FLUORINE ADDED TO SOIL	AVERAGE DRY WT OF PLANTS	FLOURINE CONTENT OF PLANTS
		ppm.	*gm.*	*ppm*
2	A	50	.46	68.0
5	B	50	.62	25.0
2	A	78	.26	111.0
5	B	78	.18	51.0
3	A	0	.45	3.7
6	B	0	.68	3.5
3	A	0	.45	4.0
6	B	0	.15	9.8

* Sassafras loamy sand of Springtown Corners, N. J., containing 12 ppm. of naturally occurring fluorine.

† Congaree sandy loam of Beltsville, Md., containing 214 ppm. of naturally occurring fluorine.

Equal quantities of NaF were stirred into unlimed plots of the sandy loam, across the aisle from the corresponding plots of the loamy sand that were a part of the preceding experiment. Two crops of collards were sown and harvested at the same time as were the first two crops of the first experiment, for comparison of the uptake of fluorine from the two soils. The data from comparable plots are recorded in table 2.

These data show that the plants took up more than twice as much fluorine from the fluorides applied to the loamy sand as from the sandy loam. For the first crop, the uptake from the two soils was 68 and 25 ppm., respectively. When the added fluorine amounted to 78 ppm., for the second crop, the plants in the sandy loam were uninjured and contained but 51 ppm. of fluorine, whereas those in the loamy sand were stunted and contained 111 ppm.

Results of a pot-culture test of the comparative toxicity of fluorine in the two soils also showed that plants tolerated much more NaF without injury in the sandy loam than in the loamy sand. Whereas in the latter soil collards were stunted by a concentration of 100 ppm. of fluorine and failed to germinate at concentrations of 400 or more ppm., those in the sandy loam were not injured at any concentration used up to 800 ppm.[5]

SUMMARY

Fifty parts per million of fluorine added as hydrofluoric acid to an acid (pH 4.9) sandy soil in small increments over a period of 6 weeks stunted collard plants to about half their normal size. Tops of the injured plants had a fluorine content of 96 ppm. In contrast, plants in limed soil took up but 43 ppm., and this was harmless.

Where sodium fluoride was added to the soil, plants from the unlimed and limed plots contained 68 and 45 ppm. of fluorine, respectively, and none were injured.

Where relatively insoluble calcium fluoride was added to the soil, still less fluorine was found in the plants—37 ppm. and 5 ppm. for the unlimed and limed plots, respectively, with no plant injury.

Analyses of a second crop of collards grown in these same plots after the soil had been remixed then given additional 2-ppm. increments of fluorine to produce a total of 78 ppm., showed more fluorine in plants that received hydrofluoric acid than in those that received sodium fluoride. Liming greatly reduced uptake of fluorine from both chemicals. Hydrogen and sodium fluorides in the unlimed plots were both highly injurious, as shown by reduced dry weights, while plants in the adjacent limed plots with their relatively low fluorine contents were uninjured.

Analyses of a third crop, buckwheat, from the same plots after additional increments of the two soluble fluorides had increased the fluorine added to the soil to 102 ppm., again showed that more fluorine was taken up from HF than from NaF, and that liming had greatly decreased fluorine uptake from both fluorides and prevented injury to the plants.

The leaf injury caused by the large fluorine uptake of the buckwheat plants in the unlimed plots was a marginal withering and chlorosis, followed by necrosis and sometimes spotting. Collard plants injured by fluorine showed similar symptoms. Buckwheat took up more fluorine than did collards and tolerated larger quantities in its tissues without injury, judged by the healthy condition of the buckwheat that contained 900 ppm. of fluorine compared with the stunted growth of three lots of collards containing but 96, 111, and 262 ppm., respectively.

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[5] Wheat, like collards, was uninjured by this concentration of fluorine, but barley showed fired leaf tips with half as much. Moreover, leaf spotting appeared on barley at concentrations of 600 ppm., but wheat in the same pots showed no injury.

The Actinomycetes. By SELMAN A. WAKSMAN. The Chronica Botanica Co., Waltham, Massachusetts, and Stechert-Hafner, Inc., New York, 1950. Pp. 230, figs. 39. Price $5.

This is volume 9 of *Annales Cryptogamici et Phytopathologici.* An introductory page presents a biographical statement on the author. The text goes into detail concerning the taxonomy, identification, morphology, mutation, nutrition, enzymology, antagonistic properties, and distribution of actinomycetes and the part these microbes play in the decomposition of plant and animal residues and as causative agents in plant, human, and animal diseases. The appendix gives the composition of media employed in the study of actinomyctes and a bibliography of 522 references, more than 50 of which are papers by the author and his associates. Anyone who is interested in this phase of microbiology will find this volume of great value.

Agricultural Progress in the Cotton Belt Since 1920. By JOHN LEONARD FULMER. The University of North Carolina Press, Chapel Hill, 1950. Pp. 236, figs. 26. Price $3.50.

The author points out that the area devoted to cotton has declined from a peak of 43.5 million acres, in 1926, to less than 25 million acres harvested annually since 1938. In contrast, the area devoted to other important farm crops, notably sorghum, hay, oats, wheat, peanuts, soybeans, rice, and vegetables, has increased from 27 to nearly 45 million acres. Similarly, the number of cattle, of which a little more than one quarter are dairy cattle, has increased from 15 to nearly 20 million. In 1924, 50 per cent of the gross farm income was from the sale of cotton, in comparison with about 25 per cent at present. In the summary, the author suggests that cotton production be standardized at around 20 million acres, that inducements be made to young men to train for agriculture, that a training program be developed for farm labor, that a national land-use policy be developed for the Cotton Belt, and that an effort be made to speed up the application of the findings of the agricultural experiment stations. The appendix contains some very useful statistics and a long list of references. The book merits wide reading by all those who are concerned with national agricultural welfare, as well as by those who live in the Cotton Belt.

Applied Sedimentation. Edited by PARKER D. TRASK. John Wiley and Sons, Inc., New York, 1950. Pp. 707. Price $5.

The 35 papers contained in this book were written by specialists in sedimentation, in engineering in connection therewith, and in a great variety of closely related subjects. Among the topics discussed are: origin of soils, landslides, permafrost, effects of soil conservation, sedimentation in reservoirs, gullying, ceramic clays, sedimentary mineral deposits, problems in petroleum geology, and some military and naval applications. These papers were prepared under the direction of the Division of Geology and Geography of the National Research Council. A long list of references is appended to each paper, the total number for the entire volume being more than 2,000. The book is well illustrated and presents a comprehensive picture of the problems involved and the methods that are being employed to deal with them. It contains a large amount of very useful information of interest to a great variety of workers in this field of research. A copy should be available for reference in every agricultural experiment station library.

The Biochemistry of Vanadium. By Didier Bertrand. American Museum of Natural History, New York, 1950. Pp. 49. Price $0.65.

This is No. 2 of the Survey of Contemporary Knowledge of Biochemistry, which constitutes article 7, volume 94, of the publications of the American Museum of Natural History. The paper was translated by Vera Lee, and the preface was written by G. E. Hutchinson, at whose invitation the paper was prepared. It discusses vanadium in rocks, sediments, waters, soils, coals, petroleum, plants, and animals. The toadstool *Amanita muscaria* is an outstanding example of a vanadium-accumulating plant, with an average vanadium content of 112 ppm. dry weight, in comparison with a mean of about 1 ppm. for other plants. The evidence strongly suggests that vanadium is essential to all plants, notably to the legumes and the nitrogen-fixing bacteria. This bulletin is highly recommended to those who are concerned with minor-element studies in relation to the growth and well-being of plants, animals, and man.

Biophysical Research Methods. Edited by Fred M. Uber. Interscience Publishers, Inc., New York, 1950. Pp. 667. Price $9.50.

One of the most interesting chapters in this book is entitled: "Avoid Fruitless Experiments." It was written by the editor and gives an excellent summary of the problems and pitfalls in research. The figures in this chapter are cartoons, and they illustrate the author's points very effectively. The remainder of the book deals with apparatus and techniques, with special reference to osmotic pressure, viscosity, temperature, colorimetric, bioelectric, and electrophoresis measurements, and to a considerable variety of other topics, including centrifugation, ultrasonic vibrations, electron microscopy, absorption spectra, x-radiation, electrons and related particles, stable isotopes, and radioactive tracers. Each chapter is written by a specialist in that field and has a long list of important references appended. The book is well illustrated with excellent drawings of the apparatus involved. The quality of the material presented is of a high order. The book fills a very important need for reference purposes.

Botany. By Wilfred W. Robbins and T. Elliott Weier. John Wiley and Sons Inc., New York, 1950. Pp. 480. Price $5.

The subtitle of this textbook is "An Introduction to Plant Science." The authors have made a very evident attempt to arouse the curiosity of the beginning student in botany who may be taking the course merely because it is required. The book first deals with the plant world in general and then proceeds to the classification of plants, a discussion of their parts, the processes that take place within the plant, and the evolutionary development of the plant kingdom. For easy reading, a double-column format was employed. Each illustration is well labeled and tells its own story, almost without reference to the text. The several hundred excellent illustrations should be of great interest to every student, no matter what his purpose in life. It is readily apparent that the authors have invested much time and energy in the development of this text, which is certain to enjoy very wide adoption by teachers of this subject.

Clinical Nutrition. Edited by NORMAN JOLLIFFE, FREDERICK TISDALL, AND PAUL CANNON. Paul B. Hoeber, Inc., New York, 1950. Pp. 925, illus. 127. Price $12.

Prepared under the sponsorship of the Food and Nutrition Board of the National Research Council, this book constitutes an authoritative presentation on diagnosis of nutritional deficiencies, malnutrition with respect to the various essential constituents, and means of control. The 36 contributors are outstanding representatives of their several fields of research, each occupying an important position in some college of medicine or institute of nutrition. The several chapters deal with methods of diagnosis of deficiencies in man, the various types of malnutrition, including those related to mineral, trace-element, and vitamin deficiencies, and the principles of nutritional therapy, including consideration of diet-otherapy, obesity, nutrition and health, nutrition in public health service, and nutritional problems associated with industrial work. The appendix contains recommended dietary allowances, food-value tables, dietary patterns, and ideal weights. The illustrations, 61 of which are in full color, are exceptionally good. The book is of much interest to soil-plant scientists who are concerned with the production of food crops of high nutritional quality. The part dealing with minerals, trace elements, and vitamins is of special importance in this connection, since these qualities of crops are susceptible to improvement by crop-production specialists. The book should be readily available to every scientist concerned with soils, plants, animals, and man.

Croissance des Végétaux Cultivés. Fourth Edition. By A. DEMOLON. Dunod, Paris, 1949. Pp. 477, figs. 98.

This book was designed for those who are concerned with research in the production of crop plants. It deals with the physical, chemical, and biological factors involved, and the growth and yield of crops. Two chapters of special importance are those concerned with crop quality and experimental procedures. The appendix outlines methods of analyses of plant materials. A list of 25 selected books and 15 periodicals for reference is presented in the front of the book, and a large number of other references are given in footnotes. Of the minor-element group, copper, zinc, manganese, and boron are discussed, with some additional comments on molybdenum for leguminous plants and cobalt for animals. Relatively little attention is paid to sodium. Rubidium and caesium are mentioned, as are the toxic elements, including zinc, copper, lead, arsenic, and vanadium. Magnesium is also discussed in this connection, with special reference to its ratio to calcium and potassium; and toxicity of selenium to livestock is mentioned. This is an excellent book for use in developing a reading knowledge of French, with definite possibilities of gaining a number of new ideas in the process.

Experimental Designs. By WILLIAM G. COCHRAN AND GERTRUDE M. COX. John Wiley and Sons, Inc., New York, 1950. Pp. 454. Price $5.75.

Statisticians do not perform experiments. They tell other folks how to do it. But this is largely for self protection. At first they merely analyzed the results of tests brought to them for interpretation. Then they decided it would help if they offered some suggestions on planning experiments so that statistical analysis could more readily be applied. That is the purpose of this book. It begins with an analysis of the principles that underlie sound experimentation. Then it discusses the most important experimental designs that have been demonstrated to have value in research programs. It serves as a handbook for consultation in planning experiments and in analyzing the data, once they have been obtained. Most of the illustrations have been taken from the field of biology, and a large percentage of these from agriculture. The book, therefore, is of special value to scientists in the agricultural experiment stations the country over. The appendix contains tables of random permutations and more than 100 selected references. Any researcher who is planning a comprehensive experiment to cover a period of years would show good judgment in consulting this book as his first step. This is the most useful book in its field so far published.

Field Crops in Colorado. By WARREN H. LEONARD AND ROBERT S. WHITNEY. Burgess Publishing Company, Minneapolis, 1950. Pp. 322, figs. 18. Price $4.

This book is unique in that it deals with field crops on a state basis rather than on a national basis. It is designed to supplement the authors' more general text, "Crop Production." Virtually all of the research reported was conducted in Colorado. The book is divided into four parts: general principles, crops of the grass family, leguminous crops, and crops of other plant families. The appendix contains weights and measures, rate of discharge of irrigation water, and silo tonnages at filling and after settling. The chapters on irrigation, sorghums, alfalfa, field beans, and sugar beets are of special interest. Included among the minor crops are safflower, flax, buckwheat, sunflowers, Jerusalem artichokes, and guayule. The book should fill a highly important place in the instructional program in Colorado and near-by states.

Foundations of Modern Physics. Second Edition. By THOMAS B. BROWN. John Wiley and Sons, Inc., New York, 1949. Pp. 391, figs. 181. Price $5.

As the title suggests, this book presents the fundamental theories on which modern physics is based. Mathematical concepts are expressed in terms of algebra and geometry. Specific experiments are described as a means of illustrating principles. The first part of the book deals with particles and waves *per se*, the second with dual wave-particle relationships, the third with the kinetic theory of atoms and molecules, and the fourth with nuclear physics, including atomic energy. Problems and references for supplemental reading are appended to each chapter. The appendixes present the units of physical measurement, physical constants, periodic tables, periods of oscillation, the theory of relativity, and the theory of radioactive decay. The illustrations are excellent. The author is to be congratulated on his ability to present a highly complex subject in a readily understandable manner. Many soil-plant scientists will find this book very useful for ready reference.

Food and People. By the United States National Commission for Unesco, Department of State, Washington, D. C.

This consists of a series of paper-bound pamphlets, including *Food, Soil, and People*, by Charles E. Kellogg; *Food and the Family*, by Margaret Mead; *U. S. Agriculture in the World Food Situation*, by Arthur P. Chew; *Food and People*, by Alva Mydral and Paul Vincent; *Distribution of the World's Food*, by Stefan Krolikowski; *U. N. Sets the Table*, by Peter Kihss; *Food and Social Progress*, by Andre Mayer; and a guide for leaders of discussion groups. The pamphlets are available free for discussion leaders. Others may purchase them from the Manhattan Printing Company, 225 Lafayette Street, New York 12. The material in these pamphlets is well presented and merits study.

Fourth International Congress of Soil Science Transactions, Volume 1. Hoitsema Brothers, Groningen, Netherlands, 1950. Pp. 428.

The editorial committee presents in this volume the three general lectures by T. Wallace, H. H. Bennett, and L. Dudley Stamp, and all or part of 108 additional papers on soil physics, chemistry, biology, fertility, and conservation, clay minerals, tropical and subtropical soils, land classification and evaluation, and saline soils. A second volume, containing the remainder of the papers, is expected to be available by the beginning of the Congress, which is to be held in Amsterdam, July 24 to August 1, 1950.

Fruit Science. By NORMAN FRANKLIN CHILDERS. J. B. Lippincott Company, New York, 1949. Pp. 630, figs. 304. Price $5.

The purpose of this book is to provide undergraduate instruction in pomology. To that end, the author has presented a comprehensive and modernized survey of the science and practice of growing and marketing fruit, including apples, pears, peaches, plums, cherries, grapes, strawberries, bush berries, and other closely related fruits. The first 12 chapters are concerned primarily with apples, and present this subject in considerable detail. It is assumed that the principles involved in the production, harvesting, storing, and marketing of this fruit can be applied, with suitable modifications, to other fruits as well. Each chapter is followed by a set of questions and a list of suggested collateral readings. The large number of excellent illustrations is a highly important part of the book. The author is to be congratulated on having brought together in one volume such a large amount of well illustrated material for the benefit of students in this field. Fruit growers will find the book highly useful for reference.

Heavy Metal Prosthetic Groups and Enzyme Action. By OTTO WARBURG. Oxford University Press, New York, 1949. Pp. 230, figs. 49. Price $3.75.

The translation from the German original was made by Alexander Lawson. The book begins with a discussion of the experiments of Edmund Davy, in 1820, which led to the discovery of the catalytic effect of finely divided platinum. It then deals with oxygen-transporting iron, the oxygen-transporting copper complex of the phenol oxidases, the hydrogen-producing iron catalyst of the butyric acid bacteria, the heavy metals of yeast zymohexase, and the heavy metals of the chloroplasts. The final chapter has to do with the quantum requirement of carbon dioxide assimilation. The book is of interest primarily to those who are closely identified with enzyme research, and the translator has rendered a high service to them.

Jan Ingenhousz, Plant Physiologist, with a History of the Discovery of Photosynthesis. By HOWARD S. REED. The Chronica Botanica Co., Waltham, Massachusetts, and Stechert-Hafner, Inc. New York, 1950. Pp. 393, illus. and plates 13. Price, paper-bound, $3.

This is number 5/6, volume 11, of Chronica Botanica. It begins with a biological sketch of Ingenhousz. It then proceeds with a discussion of his studies which led to the discovery of photosynthesis. Finally, it gives the text of 18 of Ingenhousz's experimental reports, with supplemental comments concerning them. The appendix contains two letters from Benjamin Franklin to Ingenhousz which indicate that these men were close friends. The contents of this volume are of great interest not only to plant physiologists but to all those who are engaged in research in that it permits of a study of the workings of a highly original mind at a time when science was in its infancy.

The Nature of Natural History. By MARSTON BATES. Charles Scribner's Sons, New York, 1950. Pp. 309. Price $3.50.

The well-trained and widely traveled author of this book brings a wealth of interesting philosophy to play in his word picture of the living world of which we constitute a part. Using the movie technique, he first takes a look at the earth whirling through space and, moving toward it, begins to pick up the details until he finally sets to work exploring as with a microscope. He finds space to consider the problem of naming organisms, cataloging nature, taking a look at biologic time, examining into reproduction, and watching the individual develop, commenting that man is the only animal that has lost the ability to grow up. Then he considers the influence of environment, the part played by community life, the despotic nature of populations, with time out to comment favorably on

Raymond Pearl and to raise an eyebrow at Vogt and Osborn, our current "prophets of gloom." Finally, he considers adaptations, the nature of evolution, natural economy, the naturalists themselves, experimental techniques, and the goal—"to learn to face the world more boldly as we find it." The appendix contains more than 60 selected references, with supplemental comments as to the special importance of each. The book is an excellent example of interesting, informative, and stimulative writing.

Out of the Earth. By LOUIS BROMFIELD. Harper and Brothers, New York, 1950. Pp. 305, plates 32. Price $4.

Louis Bromfield makes such a good case for his methods of research as almost to persuade one that the experiment stations have the wrong approach to the study of soils, plants, animals, and man. Of course, Bromfield is an intelligent man, and he reads, travels, and talks to many persons in the course of a year, most of whom apparently come to visit him. As a result of his many contacts he is becoming an increasingly well-informed man, and this book shows it. Thus he no longer advocates throwing away the moldboard plow, eliminating the corn crop, farming without fertilizers, specializing in earthworm production, or doing a lot of other things that passing fancies suggest, but he puts each of these in its proper place. And he raises some very embarrassing questions for agricultural scientists to ponder, such as his method of curing cattle of Bang's disease. All of this is set down in print in such an attractive manner that the reader finds himself entranced by the good earth as Bromfield portrays it. The book is worth having.

Periodic Acid and Iodic Acid and their Salts. Fifth Edition, revised. By G. FREDERICK SMITH. The G. Frederick Smith Chemical Company, Columbus, Ohio, 1950. Pp. 108, figs. 2.

"Periodic acid or its alkali salts are reduced in aqueous media to iodic acid or iodates by certain organic compounds in accordance with quantitative reactions which make possible the determination of the reducing agents." This statement, quoted from an introductory note by L. Malaprade of the University of Nancy in France, who first made use of this principle, gives a general idea of the purpose of the book. The several chapters deal with nomenclature, preparation of reagents, methods of determination of manganese in various materials, of potassium and lead, and of arsenic, antimony, iron, thallium, thiocyanate, sulfurous acid, hydrogen peroxide, and hydrazines, and reaction characteristics in the oxidation of organic compounds. A bibliography of important references is appended. Analytical chemists will find much material of value in this highly specialized little volume.

Physical Methods of Organic Chemistry. Second Edition. Edited by ARNOLD WEISSBERGER. Interscience Publishers, Inc., New York, 1949. Pp. 1072. Price $12.50.

In this new edition of the first of a two-volume treatise on techniques in organic chemistry, five chapters have been added and considerable expansion is noted in a number of other chapters, some of which have been entirely rewritten. The volume gives methods of determining melting, freezing, boiling, and condensation temperatures, vapor pressure, density, solubility, viscosity, surface tension, osmotic pressure, and contains chapters on calorimetry, microscopy, determination of crystal form, crystallochemical analysis, and determination of the properties of monolayers and duplex films. General references are appended to each chapter and more specific ones are shown as footnotes. The volume is well illustrated with good diagrams. The writers are widely known for their contributions in their respective fields of research. As in all compilations of this type, there is considerable variation in the quality of writing, but most of the material is presented in excellent form. The volume is certain to find wide usage among and save a lot of time for organic chemists who need to use physical methods in their work. Every organic chemistry laboratory will want a copy of the book close at hand for ready reference.

Reconnaissance Soil Survey of Japan, Kyushu Area. By ROBERT E. O'BRIEN AND E. J. KOHLER. General Headquarters Supreme Commander for the Allied Powers, Tokyo, 1950. Pp. 73, figs. 12, colored maps 10.

This is multigraphed report No. 110-B of the reconnaissance soil survey of Japan. It covers the island of Kyushu, the southernmost of the four main islands. Much of the area is mountainous, the agriculture is largely rice culture, the farms are very small, most of the work is done by hand, and the climate is humid and subtropical. For the most part, the soils are of volcanic origin and comparatively young, the crop lands are alluvial, and the cultivated soils are developed from windblown volcanic ash. The report is well illustrated and very interesting. It gives a very good picture of a highly intensive type of agriculture, in addition to describing the soils of the area.

Soils, Their Origin, Constitution, and Classification. Third Edition. By GILBERT WOODING ROBINSON. Thomas Murby and Co., London, 1949. Pp. 573, figs. 22, plates 9. Price 32s.

The purpose of the author is to present a general view of the science of pedology. With each revision, the book has been enlarged and its scope has been extended. Appended to the introductory chapter is a considerable list of important reference books and journals. The second chapter gives a general view of the soil and its constituents. It is followed by chapters on soil formation, clay complex, base exchange, organic matter, physical properties, water relationships, podzols and chernozems, hydromorphic, saline, tropical, and calcareous soils, classification, geography, surveys, and analysis of soils, and, finally, soils in relation to agriculture. Important references are appended to each chapter. Some very interesting and instructive profiles are presented as plates. The book is dedicated to C. F. Marbut and it shows considerable evidence of his influence on the author. Every student of the science of pedology will find much of interest and value in this presentation.

Survey of Literature on the Influence of Ions on Plants and Soils. Compiled by A. MIRASHAN. Interscience Publishers, Inc., New York, 1948. Pp. 46. Price, paper-bound, $1.25.

This survey was made under the auspices of the Board for Scientific and Industrial Research of the Government of Palestine. The subject is considered largely in relation to the problem of salinity and the need for some method of desalting the irrigation water. Reference is made to 92 papers on related topics. In addition to the common methods of overcoming salinity, the suggestion is made that improvement may be effected by addition of fertilizers. There is evidence of the value of this method. The assumption is that deficiencies of certain elements, rather than high salt content, may be responsible at times for the crop's failure to grow satisfactorily.

Teaching Agriculture. By CARSIE HAMMONDS. McGraw-Hill Book Company, Inc., New York, 1950. Pp. 353, figs. 8. Price $3.50.

The author of this book is thinking primarily of teachers of agriculture rather than professors of specific subjects in a college of agriculture, but one chapter is devoted to the needs of the latter group. His purpose is to present a background of educational concepts, together with some of the philosophy and psychology of teaching. He is disturbed by the extent to which farm folks move to town and take their money, or their training which represents money, with them. To compensate, he favors subsidizing education in agriculture. It is comforting to note that a man of 60 has a learning capacity equal to that of a 20-year-old. The book contains a considerable amount of very useful and suggestive material. It would be greatly improved, however, by more illustrative material, notably graphs.

THE EDITORS.

Thermal Properties of Soils. By MILES S. KERSTEN. Bulletin 28, Engineering Experiment Station, University of Minnesota, St. Paul, 1949. Pp. 227, figs. 138, plates 5. Price $2.

This report presents the results of investigations to determine the thermal properties of a number of soils under varying conditions of temperature, moisture, bulk density, and texture. The term "soils" is here used in the engineering sense. Notwithstanding this limitation to the agricultural soil scientist and even though all but three soils (two from Minnesota and one from Massachusetts) were from Alaska, these studies have considerable value in that they were designed to establish fundamental laws and relationships. Numerous well-drawn graphs make for an excellent presentation of the data. Four charts aid in the prediction of conductivity values for other soils.

GEORGE R. BLAKE.

NOTE

The Texas Research Foundation of Renner, Texas, announces that it has been appointed the agency to receive nominations for three awards to be presented biennially by the Hoblitzelle Foundation on a state and national basis "to encourage the development of well-balanced efficient agricultural systems adapted to the soils and climate of the respective regions." These awards are for the person who has made the most important scientific contribution to American agriculture; the Texan who has made the most important scientific discovery or contribution through investigations conducted largely or wholly in Texas; and to the Texan who has made the most notable contribution to the advancement of agriculture in Texas. Each award consists of a gold medal and $5,000.

Gilbert Wooding Robinson

SOIL SCIENCE

VOLUME 70 *September 1950* NUMBER 3

Gilbert Wooding Robinson

1889–1950

Dr. Gilbert Wooding Robinson, C.B.E., F.R.S., professor of agricultural chemistry and dean of the Faculty of Science in the University College of North Wales, died suddenly on May 6, 1950, at the age of 61.

Professor Robinson was a native of Wellington, Shropshire, and was educated at Wolverhampton Grammar School and Cambridge University, where he was a scholar of Gonville and Caius College. After a short period as demonstrator in the School of Agriculture of that university, he was appointed advisory agricultural chemist at the University College of North Wales in 1912. He was appointed independent lecturer in 1920 and made professor of agricultural chemistry in 1926. For many years he was chairman of the Soils Correlation Committee of the Ministry of Agriculture, and in 1939 was appointed the first director of the Soil Survey of England and Wales, a post he held until 1946, when reorganization of the Agricultural Services resulted in transfer of the survey headquarters to Rothamsted. He then became chairman of the Soil Survey Research Board of the Agricultural Research Council, which enabled him to keep in close touch with that branch of soil science that had interested him most. This also gave the survey the great benefit of his long and extensive experience. He was an active member of the International Society of Soil Science and had been president of Commission I (Soil Physics) since 1930. He had also been president of the British Soil Science Society since 1948. In 1936, he became a consulting editor of SOIL SCIENCE. For his contribution to pedology he was made a Fellow of the Royal Society in 1948.

He was one of the very few Englishmen who have taken the trouble to master colloquial Welsh, in which he frequently lectured and broadcast. This kept him in close touch with the farming community, by whom he was held in great respect. He also took a deep interest in Welsh national affairs, especially education, and was a prominent churchman. He was a Justice of the Peace for Caernarvonshire, and in 1948 was made Commander of the Order of the British Empire.

He had an excellent command of languages, speaking six fluently, was widely traveled, and had many friends in all parts of the world. In 1949 he visited New Zealand as a Royal Society delegate to the Seventh Pacific Science Congress, an opportunity he used to become familiar with some of the soils of that country and Australia. For a long time he had a close association with Spain, where he gave a course of lectures in 1946, and his translation of del Villar's book on the soils of Spain is well known. Only recently had he returned from a visit to that country after receiving a gold medal on his election as an honorary member of the Spanish Higher Council of Scientific Research.

About the time Professor Robinson was studying at Cambridge, a great interest in soil survey developed in Great Britain and in particular at that university. Within a few years reports appeared on the soils of Dorset, parts of Cambridgeshire, and, of course, the well-known "Soils of Kent, Surrey and Sussex" by Hall and Russell. Robinson's contribution to this early work was his survey of the soils of Shropshire (1912). This interest in soil survey he took with him to Wales, and a steady, although not large, stream of papers on the soils of North Wales came from his pen.

In an interesting contribution to Commission V of the Comité International de Pedologie in 1924 he provided a brief account of the development of his ideas on soil survey and soil classification. The early work had tended to emphasize the close relation that exists between "solid" geology and soils in the nonglaciated regions of England, but farther north, in Shropshire, his survey convinced him that matters were not quite so simple where glacial drifts, sometimes far-traveled, gave a somewhat different picture. In Wales the position was even more complicated.

The ideas of the Russian school gradually spread after the first World War, and he quickly realized that these would provide a solution to the problem of soil classification. In the 1924 paper he indicated, rather diffidently, one feels, that there are podzols in Wales and that the calcareous soils of the south of England might be considered as rendzinas.

A beginning was made with a systematic and detailed soil survey of Wales under his direction in 1925, and in spite of the small staff, good progress was made. The classification used in the early stages was based mainly on surface texture and geology, but in 1929 he decided to adopt the American system of soil series and types based on the soil profile, which through his influence as chairman of the Soils Correlation Committee has been generally used since that time in England and Wales.

During the First International Congress of Soil Science, he came under the spell of C. F. Marbut, and the dedication of "Soils, Their Origin, Constitution and Classification" indicates how much he owed to this friendship. The book, however, showed an originality of outlook and presentation that has made it one of the best texts on pedology and one that will not lose its value for many years to come.

The early soil surveys showed the need for more satisfactory methods of soil analysis, and the Robinson procedure of mechanical analysis, which masquerades under the title "International Method," is now the standard method in most laboratories. The preparatory investigations for this led to some interesting work by Robinson and his colleagues on the effect of hydrogen peroxide on soil organic matter, and he evolved an ingenious method of determining carbon and nitrogen on the same sample of soil. He was one of the leading exponents of use of the composition of the clay fraction in the soil profile as an aid to elucidation of the nature of the pedogenic process and to soil classification.

It is to Robinson's teaching and lecturing that we must look for his major contribution to the development of soil studies in Great Britain and elsewhere. His broad outlook and genial nature made him an ideal lecturer, and he was always ready with sympathy and counsel for students and younger workers struggling with the rapid and rather specialized advances in soil science. His students are to be found not only throughout Wales, but in most agricultural teaching and advisory centers in Britain, and many are in the Colonial Agricultural services.

His modesty and ability to see other points of view are well illustrated in the preface to his book, where he quotes Cervantes, *"He propounds something and concludes nothing."* Readers of "Soils" will realize how far from the truth this is. His ready grasp of the essentials of an argument made him a most valuable speaker in any discussion.

His early work had an essentially practical bias, but later his profound knowledge of the classics led him to a more philosophical approach to pedology, which is well illustrated by his last contribution to the British Journal of Soil Science. Nevertheless, his continued appreciation of the needs of practical agriculture was shown during the recent war in the great service he rendered on the various committees dealing with the problems of increasing food production.

Soil science has suffered a very great loss in Professor Robinson's death, but we hope that the soil survey he strove so hard to build up will continue to serve as a living tribute to his memory.

ALEX MUIR

RELATIONS OF SOIL AIR TO ROOTS AS FACTORS IN PLANT GROWTH[1]

J. B. PETERSON

Purdue University Agricultural Experiment Station

Received for publication December 13, 1949

As techniques for growing plants in soil in the field have improved, failure to reach expected levels of productivity with new varieties, despite adequate application of essential nutrients and of weed, insect, and disease controls, has focused attention on the significance of physical properties of soils.

In handling field soils, farmers simply expedite a few steps in the great natural hydrologic cycle to provide the roots of their crops with a proper air-water environment. Water from the earth's surface is pumped into the air by the sun's energy and is brought to the field under the indirect influences of this energy, the motion of the earth, and gravity. As precipitation, it is available to plants only if induced to soak into the soil rather than run off the surface. Once in the soil, excess water must be carried on down and out by gravity to prevent clogging of the pores and injurious exclusion of air.

The farmer may control applications of water through irrigation. Where he can do this and where water and fertilizer are cheap, sandy lands are desirable because of their high porosity, rapid drainage, and good aeration.

Where water is expensive or is obtained only from precipitation, the capacity of the soil to hold enough usable water to keep growth at a maximum between additions becomes important.

The subject of soil aeration has been well covered by numerous reviews, among which those by Page,[2] Kramer (35), Baver (5, pp. 267–287), Miller (39), Meyer and Anderson (38), the Cornell University Interdepartmental Seminar,[3] and Clements (19) are especially useful.

EFFECT OF AERATION ON CROP RESPONSE

There is ample evidence of the plant's need for oxygen in soil air and of the harmful effects of inadequate supplies of this material. Yields of tomatoes in water culture were materially increased by aeration of the solution (3). Aeration produced increases of as much as 210 per cent in tomato yield from culture solution (18). Increasing the noncapillary pore space has reduced loss of stand of sugar beets and increased yields on silty clay loams and clays of northwestern Ohio. Where soil aeration was improved, yields were increased threefold to fivefold (4). In this same study a total air capacity of 2 per cent by volume produced short stubby beets, whereas a capacity of 8 per cent resulted in long tapering beets. Corn (33), *Impatiens balsamina* (28), and apple seedlings[4] are among the crops for which definite response to soil aeration has been found. Other examples of the beneficial effect of adequate aeration on yield have been reported by Stiles and Jorgensen (49) for barley and balsam, by Clark and Shive (18) for tomatoes, and by Allison and Shive (1) for soybeans.

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[1] Journal Paper No. 469 Purdue University Agricultural Experiment Station, Lafayette, Indiana. Contribution from the department of agronomy.

[2] Page, J. B., and Bodman, G. B. Effect of soil physical factors on nutrient availability. Univ. Wis., Madison, Centennial Symposium on Mineral Nutrition of Plants, 1949. [Unpublished.]

[3] Cornell University Aeration and plant growth. Rpt. of Interdepartmental Seminar, 1947. [Mimeo.]

A typical growth response to soil oxygen is shown in figure 1.

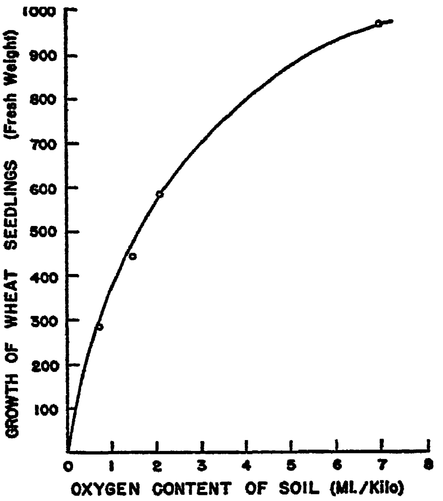

FIG. 1

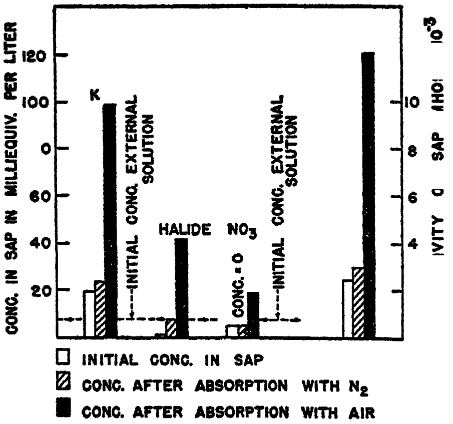

FIG. 2

FIG. 1. RELATIONSHIP OF OXYGEN CONTENT OF SOIL TO GROWTH OF WHEAT SEEDLINGS
From Karsten (32); reproduced by courtesy *American Journal of Botany*

FIG. 2. EFFECT OF AERATION ON ACCUMULATION OF SALT BY EXCISED ROOTS OF BARLEY
From Hoagland and Broyer (26); reproduced by courtesy *Plant Physiology*

PHYSIOLOGICAL EFFECTS OF SOIL OXYGEN

The beneficial effects of soil oxidation may be due to stimulation of root growth (15). This stimulation may express itself in greater root branching, length, area of root surface; more root hairs; and thicker roots (1, 13, 15, 17, 20, 23, 49), all of which would result in greater feeding power of the plant.

Bryant (13) observed that the cortex of roots in aerated solutions had uniformly compact parenchyma with no intercellular spaces. That of nonaerated roots had large air passages separated by narrow strands of parenchyma. Starting at 25 mm. from the root tips, the cell walls of aerated roots thickened more rapidly than did those of nonaerated roots. Tissues of nonaerated roots started to differentiate nearer the tip than those of aerated roots. Compton[5] pointed out that this gave the aerated roots a greater effective feeding area in the root zone where most active salt absorption had been observed (41).

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[4] DeVilliers, J. I. 1939 Some responses of MacIntosh apple seedlings growing with the roots in various concentrations of oxygen. 1939. [Unpublished thesis for Ph.D. Copy on file Cornell Univ., Ithaca, N. Y.]

[5] See footnote 3.

Early work such as that of Hoagland and of Steward and their respective coworkers (8, 26, 45, 46) yielded evidence that salt accumulation by storage tissues (defined by Hoagland and Broyer as "movement of cations and anions into the vacuole against concentration gradients") was dependent upon metabolic activities of living cells as reflected in aerobic respiration.

Steward (46) proved that accumulation of potassium salts by discs of storage tissues occurred only when oxygen was supplied at a suitable tension and rate of flow. Active aerobic respiration was found to be essential. Rosenfels (42) found rapid accumulation of bromine by Elodea in the dark to depend on aeration. In the light both Elodea and Nitella obtained the necessary oxygen from photosynthetic processes.

Evidence of the relation of aeration to salt accumulation by roots is shown in figure 2. Hoagland and Broyer (26) found that potassium, bromine, and NO_3 would accumulate rapidly in the root sap against steep concentration gradients when a stream of air was passed through the external salt solution. From their results and those of Steward *et al.* (44, 46), they concluded that for the kinds of tissue studied, CO_2 production reflected metabolic activities essential to salt accumulation.

Besides evidence that the energy provided by respiration is necessary for roots to accumulate salts against energy gradients, there is evidence that certain ions stimulate respiration. This is true of potassium absorbed by potato discs (48). Thus it would seem that when potassium is present, it stimulates the respiration necessary for its accumulation. At any rate, a high rate of respiration goes hand in hand with potassium accumulation, and without that respiration, potassium is not absorbed.

Steward and Preston (48), studying the effect of a range of salt concentrations on respiration and metabolism of potato discs, used bromides, chlorides, and nitrates of potassium and calcium. Increased external concentrations of potassium salts increased respiration, protein synthesis, and other reactions favored by oxygen. Corresponding concentrations of calcium salts with a common anion depressed these processes.

The effective ions of the salts were found to be the cations. The specific effects of the cations were accentuated by the anions, order of influence of the anions on the absorption of a common cation being $NO_3 > Cl > Br > SO_4$.

In investigating relative influence of ammonium and nitrate salts as sources of nitrogen for barley plants under different environmental conditions, Arnon (2) found that plants supplied ammonium nitrogen were equal to those receiving nitrate nitrogen provided the former were grown in well-aerated solutions and manganese, copper or certain other metals were supplied. These results led him to speculate that the beneficial results of nitrate in culture solutions may be due in part to action of the nitrate as an oxidizing agent in the plant. He pointed out that nitrate was a very effective oxidizing agent, oxidizing two carbon atoms for every NO_3^- reduced to NH_4^+ with a release of 162,000 calories.

He also noted that all the metals which benefited the plants receiving ammonium were capable of assuming several valence levels and hence were suitable catalysts for oxidation-reduction processes.

Investigating this problem further, Gilbert and Shive (24) suggested two sources of CO_2 from respiration: first, the CO_2 produced by normal aerobic respiration in which the hexose substrate is completely broken down to CO_2 and H_2O; and second, "extra CO_2" which is produced from the partial oxidation of sugars in nitrate reduction. Since the first process is aerobic, the CO_2 produced should theoretically be zero at zero oxygen tension. Theoretically, this aerobically produced CO_2 should reach its maximum when oxygen is plentiful. "Extra CO_2" was found to be inversely related to the oxygen tensions of the substrate. "Extra CO_2" was determined by calculating for a given oxygen tension the difference between the CO_2 evolution of corresponding plus-NO_3 and minus-NO_3 cultures. The close relationship of this extra CO_2 to NO_3, absorbed and the influence of oxygen levels on the process is shown in figure 3.

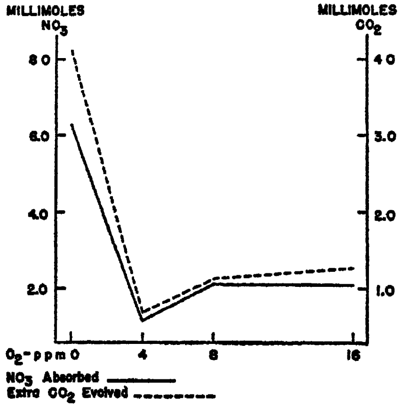

FIG. 3. RELATION BETWEEN RATES OF NITRATE-ION ABSORPTION AND EXTRA CO_2 PRODUCTION BY SOYBEAN ROOTS AFTER 23 DAYS OF TREATMENT AT FOUR OXYGEN LEVELS

From Gilbert and Shive (24)

OXYGEN REQUIREMENTS OF PLANTS

There is not complete agreement on the oxygen level needed by different plants. It may vary with the soil and the plant. Steward and Berry (47) varied the oxygen percentage in the gas above the solution in which storage tissue was submerged. They found 20 per cent oxygen was maximum for accumulation of potassium, whereas 3.8 per cent permitted 70 per cent efficiency of potassium accumulation. But at 1.4 per cent oxygen, potassium was lost from tissue to the solution. Excised roots lost potassium to solutions under partial oxygen pressures of less than 1 per cent but showed nearly maximum accumulation at 2.7 per cent. Roots of most plant species were found (15) to require as little as 0.5 per cent oxygen in soil air for survival but needed 2 to 8 per cent for maximum growth, depending on the species and conditions. The rate of oxygen supply was more important than the partial pressure *per se* in influencing the rate of growth. Wheat germination was reported reduced by oxygen pressures of 5 per cent, the reduction going to 50 per cent of normal when the pressure was lowered to 1 per cent (51). Chang and Loomis (16) concluded from reviewing the literature that plant roots would develop and function normally with 5 to 10 per cent oxygen maintained in soil gases and would survive at oxygen percentages as low as 1 to 2.

Cannon (15) found a close relation between the degree of aerobism of a species and the soil aeration of its native habitat. *Baccharis viminea, Salix lasiolepis,* and other plants normally found in soils saturated with water part of the year were able to maintain root growth at the low concentration of 0.5 per cent oxygen in the soil atmosphere. No species that required a relatively high percentage of oxygen was found in such moist habitats.

Certain swamp species have developed just as large root systems in continuously saturated as in alternately saturated and drained soils (53). On the other hand, blueberries, although native to bogs, sometimes have shown injury from lack of oxygen (22). In experiments by Girton (25), orange roots stopped growing with 1.2 to 1.5 per cent oxygen and were retarded with 5 to 8 per cent at 28° C. Apple roots were observed (10) to need 10 per cent oxygen for good growth. They could exist with 0.1 to 0.3 per cent and would grow slowly with 0.1 to 3.0. More oxygen is needed at higher temperatures than at lower temperatures (14). The effect of lower oxygen levels is more pronounced at higher temperatures. Consequently, good aeration is essential for good crop growth through hot weather.

Excessive oxygen is sometimes toxic (35). In some tests it has decreased the size of bean and sunflower plants (37). The optimum oxygen requirement of soybeans has been reported to be lower than the oxygen level in normal atmosphere, and higher concentrations have been reported to be toxic (35). Tomatoes, on the other hand, were found to thrive on twice a normal oxygen concentration (23).

HARMFUL INFLUENCE OF EXCESSIVE CO_2

Wollny (54, 55) found that the CO_2 content of soil air would increase 10 times as the moisture content changed from 6.8 to 26.8 per cent. Granular soils were found to have less than half as much CO_2 as powdery soils. The relative amount of CO_2 in the soil air increases with an increase in depth and with density and compaction of the soil (5, pp. 267–287). The proportion of CO_2 decreases with increase in number of large pores and ease of renewal of soil air.

The CO_2 and oxygen content of soil air will show wide variation within the pores of various soils, depending on soil conditions. Any soil property resulting in large air capacity, such as granular structure, will result in lower CO_2 and higher oxygen.

Thus the relation between soil, oxygen, and CO_2 content is somewhat reciprocal.

In poorly aerated soils, decrease in oxygen content is accompanied by increase in CO_2 because the conditions that restrict diffusion and interfere with oxygen replenishment also restrict removal of CO_2 produced by roots and microorganisms. As a result, it is difficult to distinguish the relative effects of low oxygen and high CO_2 in a poorly aerated soil.

Chang and Loomis (16) recognized this difficulty and stated it succinctly:

> Atmospheric oxygen is depended upon as an ultimate hydrogen acceptor in the respiration of higher plants. We must assume, therefore, that soil or cultural aeration is beneficial at minimal oxygen levels because it replaces this element. At the same time possible toxic accumulations of CO_2 are swept away. The problem, therefore, is one of minimum oxygen levels, maximum CO_2 tolerance, and expected gas concentrations around the roots of plants growing in various environments.

They found that bubbling CO_2 through water cultures for 10 minutes out of each hour reduced by 14 to 50 per cent the absorption of water by roots. The effect of CO_2 seemed to be on the water-absorption mechanism rather than on transpiration, a conclusion also reached by Kramer (34).

The effect did not seem to be due to acidity, because adding H_2SO_4 to bring the solutions to the pH reached with CO_2 had no effect on water absorption. Carbon dioxide treatment also reduced the absorption of five nutrients, the relative extent of the effect being in the order $K > N > P > Ca > Mg$. Potassium was even excreted from the roots of many plants treated with CO_2.

There is strong evidence of a direct toxic effect of CO_2 on both plant and animal protein (16, 29, 52).

Chang and Loomis (16) concluded from studying the literature on reasons for the toxic effect of CO_2 that a combination of rapid penetration of protoplasmic membranes; increases in cellular activity; and formation of specific, but weakly bonded, protein compounds is the best available explanation of CO_2 toxicity. This seems to imply the presence of a compound in living cells which becomes toxic above a threshold concentration. They suggested the formation of hydrogen-bond linkages on non-alpha-amino nitrogen which would allow a reversibility of toxic results as well as specific differences in CO_2 toxicity which have been noted. The fact that CO_2 increases the viscosity of protoplasm (21) indicates a possible effect on molecular structure.

Cannon (15) reported threshold values of CO_2 concentration at 25 per cent for many roots. He found willow growing in 45 per cent CO_2 and a normal oxygen level. Even with high oxygen levels, 20 to 30 per cent CO_2 was toxic to barley (35). For narcosis, 10 per cent CO_2 was minimum (43). Chang and Loomis (16) estimated that concentrations below 10 per cent CO_2 in soil gases were probably not highly toxic, whereas concentrations above 15 to 20 per cent were lethal to most plants.

Chang and Loomis summarized the practical importance of CO_2 toxicity under three headings: (*a*) Plant roots vary in their sensitivity to CO_2, (*b*) typical soils are low in CO_2 and high in oxygen, (*c*) a high concentration of CO_2 in the soil air depends on rapid production of the gas and a low rate of gas exchange.

They surmised that slightly toxic CO_2 concentrations of 10 to 12 per cent may be more frequently the cause of crop reduction on poorly aerated soils than are limiting concentrations of oxygen.

AVOIDING POOR AERATION THROUGH SOIL MANAGEMENT

Soils with clay in them must be so handled as to maintain enough large pores to provide adequate oxygen for roots and allow the escape of harmful amounts of CO_2 through diffusion. As pointed out by Baver (5), a clay soil will have a sufficient number of large pores to provide a satisfactory air capacity for plant growth if the soil is well granulated. Granules smaller than 0.5 mm. were found to have an air capacity of 2.7 per cent in contrast to 29.6 per cent for granules of 1.0 to 2.0 mm. (5). This means that practices which build good structure should be followed. Those which destroy structure should be avoided.

Practices that increase aeration of heavy soils by mechanical loosening are generally considered not permanent. They often have been questioned because after their use on soils in poor physical condition, the structure soon has become compacted again. Developments in traction equipment that increase the efficiency and economy of operating such special tools as those designed to open tight lower layers may make such practices feasible under more general conditions. Such machines are worthy of intense research as to design and effectiveness.

The effects of preparing too fine a seedbed are known. Soil structure deterioration through continuous row cropping with its attendant intense cultivation is accepted as an honest generalization. Beneficial effects of plowing in comparison with other ways of preparing land on some of the heavy soils in Iowa have been attributed to better aeration resulting from that method (9, 17, 36).

Comparisons of the effects of plowing, hard-ground listing, subsurface tillage, and disking on the yield of corn for 52 fields on 11 soil types in Iowa over a 3-year period showed that the average yields were significantly in favor of plowing (17). Results, however, showed considerable variation caused by differences in erosion, crops, climatic conditions, and past management. For example, the yield on the hard-ground-listed plots was 1.2 bushels more than that on plowed plots on Marshall silt loam in 1944. In 1945, yields of corn on plowed plots were 4.2 bushels higher than those on hard-ground-listed land.

Because corn on land prepared by listing, disking, and subsurface tillage was lower-yielding than that on land prepared by plowing and showed nutrient-deficiency symptoms, whereas corn on plowed ground did not, fertilizer tests were made using field plot techniques (9). These showed increases for all the plots except those prepared by plowing. Suspecting the cause to be poor aeration, Lawton (36) tested the effect of aeration on the absorption of nutrients by corn under different degrees of wetting and compaction. Increasing the soil moisture decreased the percentage of potassium, nitrogen, calcium, magnesium, and phosphorus in the corn. Compacting Clarion soil decreased the percentage of potassium and phosphorus in the corn and increased the percentage of calcium, magnesium, and nitrogen. Packing Clyde soil lowered the percentage of potassium, magnesium, and calcium in plant tissue and increased the percentage of nitrogen and phosphorus. Plant growth was reduced by every treatment that caused poor aeration of the soil.

Use of organic matter and ridging of the rows greatly improved the aeration of sugar beet land on Brookston clay in northwestern Ohio (4).

After reviewing various tillage experiments throughout the country, Baver (5) concluded that plowing sod crops for corn usually gave better yields than other methods of preparation. He admitted that any generalizations should be tempered with consideration of the kind of sod, soil, and climate.

Cultivation destroys aggregation and reduces the number of noncapillary pores. This fact is so well known that documentation seems superfluous. Good examples of supporting data, however, are those of Jenny (30), Bradfield (11), and Swanson and Peterson (50). Direct applications of organic matter and the growth of grasses and legumes are possibly the most effective practical measures known for improving soil structure and aeration. Grasses are probably most effective for surface soils; deep rooted legumes, for subsoils. There is ample evidence of the beneficial effects of such crops on soil aggregation and porosity. For example, data from the soil erosion experimental stations operated cooperatively by various states and the Soil Conservation Service universally show marked increases in the percentage of large water-stable aggregates and in infiltration capacity and decrease in surface runoff when organic matter is added or sod crops are used (7). Increases in aggregation or infiltration or both are good evidence of improved soil porosity. Typical of the data are those from Guthrie, Oklahoma:

	Runoff, percentage of precipitation
Continuous cotton	14.22
Cotton in rotation	12.72
Wheat in rotation	13.93
Sweet clover in rotation	8.00
Average of rotation	11.5

Experiments with different cropping patterns on Marshall silt loam in southwestern Iowa produced results which most likely are due in part to increased soil porosity[6]. Continuous corn from 1931 to 1947 resulted in an average yield of 22.5 bushels, whereas a rotation of corn–oats–red clover yielded an average of 81.8 bushels of corn. Reporting the effects of 10 years of cropping at the same station, Johnston and colleagues (31) stated that aggregation was improved by cropping systems, the order of effectiveness of different crops being bluegrass, clover, oats, rotation corn, and continuous corn.

In Paulding County, Ohio, Nappanee silty clay loam went from a porosity of 60 per cent to 51 (40). Page and Willard found that pore space and aggregation on these soils were limiting factors in plant growth. Poor physical conditions, which almost completely limited plant growth, were remedied by return-ing organic matter regularly to the land and by introducing sod crops in the rotation. The greatest improvement resulted from deep-rooted legume and grass mixtures.

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[6] Report of studies at the soil conservation experimental farm, Page County, Iowa, for 1943–1947. Iowa Agr. Exp. Sta. and Soil Cons. Serv. Mimeo. 88. 1948.

The effectiveness of sod crops in increasing the porosity of heavy soils in northeastern Indiana was noted by the author in a recent tour of farms where good rotations had been adopted. Using the soil sampling tube and chalk suspension test, developed by Hoffer (16) to locate compaction in the upper 18 inches, the author found that wherever sweet clover or grasses or both had been grown the dense, compact plow sole common to the area had disappeared. The results were reflected in higher crop yields and by the fact that most of the farmers using good rotations had switched from fall to spring plowing, a practice which their neighbors did not believe could be followed.

Knowledge of crop improvement through better varieties and proper fertilization is rapidly advancing. Many operators are applying this new knowledge, only to find their yields disappointing because of neglect of soil practices that ensure good structure and aeration in heavy soils. Better varieties and top fertilizer applications are ineffective where roots must grow in poorly aerated conditions. Effective diagnostic methods that help in quickly spotting compaction and poor aeration have been developed by Hoffer (6, 27). By use of such techniques the farm operator can readily spot compaction and anaerobic conditions on his soil. To the best of our present knowledge the surest remedy for such conditions is a good crop rotation including a legume-grass mixture. Grass is very effective in promoting granulation of heavy surface layers. Deep-rooted legumes, such as sweet clover or alfalfa, are needed where the subsoils are tight. Whether the deep-rooted legumes alone are capable of keeping heavy soils in good physical condition is debatable. In Ohio a combination was found best (40). There is no doubt that the man who uses a mixture of deep-rooted legumes and grasses is not taking chances on his cropping system from the standpoint of its effect on the physical conditions of his soil. Such a cropping program will be effective only when used as a part of a complete soil management program in which adequate provision has been made for necessary drainage, erosion control, liming, proper fertilization, and use of organic matter.

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UTILIZATION OF NITROGENOUS COMPOUNDS BY PLANTS

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Received for publication December 29, 1949

During the degradation in soil of nitrogenous organic residues to simple inorganic compounds, a large share of the nitrogen must pass through the amino-acid stage (6, 11). Hence, it is of interest to determine the ability of plants to utilize amino acids singly or in combination as their sole source of nitrogen.

The extensive early literature describing the utilization of organic nitrogenous compounds by plants has been reviewed by Hutchinson and Miller (5) and by Brigham (2). They pointed out the necessity for performing experiments on the nitrogen nutrition of plants under aseptic conditions and indicated which of the earlier reports were questionable because of failure to observe aseptic precautions. In these early experiments, a few amino acids in addition to a great variety of other organic nitrogenous compounds were tested as sources of nitrogen for plants.

Following these papers, several other reports concerning the availability of amino acids for plant growth have appeared. Crowther (3) observed in nonaseptic experiments that both barley and white mustard grew better on glycine than on sodium nitrate, but other amino acids were inferior to nitrate. Tanaka (16) found that plantain, mustard, and "blue eyed grass" could use urea, asparagine, acetamide, and glycine, but none was so effective as nitrate. Virtanen and Linkola (19) reported that both the D and L forms of aspartic and glutamic acids are used by peas and clover; they are taken up intact by the plants, and if aspartic acid, nitrate, and ammonia are supplied together they are used simultaneously. Wheat and barley, however, were unable to use aspartic or glutamic acids as nitrogen sources.

White (20) found that arginine, valine, proline, norleucine, tryptophan, alanine, and hydroxyproline when supplied singly depressed the growth of excised tomato roots: hydroxyproline was the most inhibitory. Robbins and McVeigh (10) likewise found hydroxyproline particularly inhibitory to the growth of *Trichophyton mentagrophytes* and certain other fungi. Robbins and Schmidt (9) could not confirm White's (20, 21) observation of a stimulation of the growth of excised tomato roots when certain amino acids, notably glycine, were added to a basal medium containing nitrate. Audus and Quastel (1) have determined the influence of a variety of amino acids and other compounds on the growth of cress roots. All the amino acids tested, except alanine and glutamic acid, inhibited root growth at 1,000 ppm. Studying the effect of 19 amino acids on growth

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[1] The authors express their appreciation to H. B. Wahlin and Warren Smith, department of physics, for mass spectrometric analyses, and to P. W. Wilson for helpful suggestions on the preparation of the manuscript. The senior author is now with Gluconate Ltd., 115 Prinsep St., Calcutta, India.

of orchid embryos under aseptic conditions, Spoerl (14) found that only L-arginine supported good growth of young embryos. Other amino acids inhibited growth, but older embryos could utilize aspartic acid. Steinberg (15) has observed that toxic effects also are induced in tobacco seedlings grown on a variety of amino acids. Particularly marked is a response to DL-isoleucine duplicating most of the symptoms of frenching disease as encountered in the field. No single amino acid supported as good growth as did the control medium containing nitrate and ammonium ions. Pratesi and Ciferri (8) observed that tobacco seedlings grew better with several single amino acids than with certain combinations of amino acids.

At the time early studies on the use of organic nitrogenous compounds were made, many amino acids were not readily available. In the present work, the growth, under aseptic conditions, of tobacco, clover, and tomato seedlings and *Chlorella pyrenoidosa* on a wide variety of amino acids was investigated.

EXPERIMENTAL PROCEDURES

Plants were grown in plain cylindrical 1.5-quart milk bottles containing 500 gm. of white silica sand and 75 ml. of nutrient solution with a given nitrogenous compound; no additional water or nutrients were supplied during the experiments. The basal nutrient solution (pH adjusted to 6.8) was: K_2SO_4, 0.0025 M; $MgSO_4$, 0.002 M; $Ca(H_2PO_4)_2$, 0.005 M; $CaSO_4$, 0.002 M; $FeSO_4$, 0.0001 M. An amount of a nitrogenous compound containing 3 mgm. N was added to each 75 ml. of the basal nutrient solution. The bottles containing sand and nutrient solution were plugged with cotton and covered with tin cans (3.5 inches high, 3 inches in diameter) to serve as dust shields; four holes 0.75 inch in diameter were punched in the sides of each can at a level below the cotton plug to permit free access of air to the bottle top. The bottles were sterilized with the cans in place by autoclaving for 2 hours at 121° C. Compounds which might be damaged by heating, such as glutamine, potassium nitrite, hydroxylamine, and the oximes of α-keto acids, were sterilized by filtration through a Seitz type filter and added separately.

The nitrogenous compounds used were Merck products except for the following: DL-serine, Gelatin Products Corp.; hydroxy-L-proline, Bios Laboratories; peptone, Difco Laboratories. Casein hydrolyzate was prepared by the method of Snell (13). The oximes of pyruvic, oxalacetic, and α-ketoglutaric acids were prepared by adding 5 equivalents of the keto acid to 1 equivalent of hydroxylamine in aqueous solution; the solution as such was used as a source of oximes.

Medium red clover (*Trifolium pratense*), John Baer variety tomato (*Lycopersicon esculentum* Mill.), and Comstock Spanish variety tobacco (*Nicotiana tabacum*) were used. The seeds were freed of microorganisms by immersion in 70 per cent ethanol for 5 minutes, sterile-water rinse, immersion for 3 minutes in sodium hypochlorite solution with 3 per cent available chlorine, sterile-water rinse, immersion in 0.1 per cent $HgCl_2$ solution for 1 minute followed by several rinses with sterile water. The seeds were treated at each stage in a vacuum desiccator; the air was evacuated and the vacuum then released to aid penetration of the disinfectants into the air pockets and under the seed coat. The tomato seeds were not treated with mercuric chloride, as this inhibited their germination; the immersion in sodium hypochlorite solution was lengthened to 5 minutes.

The surface-sterilized seeds were transferred aseptically to moistened sterile blotters in petri dishes and incubated at 30° C. until the clover and tomato seedlings were about 10 mm. long and the tobacco seedlings 5 mm. Eight clover, five tobacco, or five tomato seedlings were transferred aseptically to the culture bottles and gently pushed under the roughened surface of the sand with a sterile metal rod. When inoculated clover plants were included in the experiment, a suspension of *Rhizobium trifolii* (Wisconsin strain 205) was added only to the bottles designated as inoculated.

The bottles containing plants were placed in the greenhouse in a randomized block design; in most experiments each block had six rows of six bottles. Each of 36 treatments had four replications; a replicate of every treatment was placed at random in each of the four square blocks. The plants were illuminated for 17 hours a day. Daylight was supplemented with 200-watt Mazda lamps in reflectors. The temperature was 70 to 75°F.

After the plants had grown for 4, 6, or 8 weeks they were harvested, washed thoroughly, rinsed with distilled water, and dried in an air stream at 65° C. In addition to dry weights, the average total nitrogen per plant was determined as a measure of growth. The total nitrogen was determined on all the plants from one culture bottle by the semimicro-Kjeldahl method (17). After distillation of the ammonia from the Kjeldahl flask, the residual sand in the flask was washed free of salts with distilled water, dried, and weighed. The weight of this sand, which had adhered to the roots of the plants, was subtracted from the initial dry weight of the plants to establish the true dry weight.

A few plant cultures were discarded because of the appearance of molds on the sand. At the time of harvest, the bottles were tested for contamination by inoculating tubes of clear broth medium (0.3 per cent sucrose, 0.1 per cent beef extract, 0.1 per cent Bacto peptone) with samples of sand from 10 per cent of the cultures picked at random. The initial sterility of the entire system was tested by adding 200 ml. of the broth medium to bottles containing seedlings and incubating these and examining them for contamination. Every effort was made to maintain aseptic conditions, and the plugged bottles were not opened from the time of planting until harvest. The procedures employed were rather uniformly successful in establishing a sterile environment for the plants, but it cannot be asserted that all microorganisms were excluded from all cultures.

Pure cultures of *Chlorella pyrenoidosa* were grown with aeration (5 per cent CO_2 in air) at 24° C. on Myers' (7) medium containing various nitrogenous compounds to replace the nitrate normally supplied. Each 50-ml. culture in a 4-ounce bottle was supplied with 8 mgm. of nitrogen. Washed inoculum was used. After 8 days' growth, the algal cells were washed by centrifugation and analyzed for total nitrogen.

RESULTS

Utilization of nitrogenous compounds by clover

Table 1 lists the average dry weight and total nitrogen (average of 32 plants pooled from four bottles) relative to clover plants grown on ammonia (the plants grown on ammonia are assigned a value of 100 for comparison with other treatments). Apparently a considerable number of single amino acids support rather good growth of young clover plants. Several amino acids were substantially better than nitrate or ammonia; alanine, asparagine, and glutamic acid were outstanding in this experiment. In other experiments, we have found ammonia and nitrate to be almost equally effective and to be surpassed only by arginine, asparagine, and glycine as nitrogen sources for growth of red clover. None of the amino acids at the level supplied was toxic to clover.

TABLE 1

Utilization of nitrogenous compounds by red clover grown under aseptic conditions

NITROGENOUS COMPOUND SUPPLIED*	DRY WEIGHT PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†	TOTAL N PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†	NITROGENOUS COMPOUND SUPPLIED	DRY WEIGHT PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†	TOTAL N PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†
No added nitrogen	90	36	Inoculated	92	67
Ammonium sulfate	100	100	DL-isoleucine	116	77
DL-α-alanine	132	145	DL-leucine	115	86
L-arginine	118	126	L-lysine	144	106
L-asparagine	153	148	Nitrate, calcium	119	128
DL-aspartic acid	98	115	Nitrate, sodium	128	109
L-cystine	63	54	DL-phenylalanine	151	96
DL-glutamic acid	152	144	DL-threonine	97	116
Glycine	122	127	DL-valine	86	94
L-histidine	141	100			

* Medium red clover plants, eight to a bottle, were supplied 3 mgm. N, as the compound listed, in 75 ml. of nutrient solution. Plants were harvested 6 weeks after planting.

† Plants grown on ammonium sulfate had 8.53 mgm. dry weight per plant and 0.272 mgm. total N per plant. Data for total N are not corrected for 0.091 mgm. N supplied by each seed.

Utilization of nitrogenous compounds by tomato

Table 2 summarizes data on the growth of tomato plants supplied a variety of nitrogenous compounds. In the second experiment, the standard deviation of the mean for each treatment is given to indicate the magnitude of the differences among replicate bottles in experiments of this type. The five plants from each bottle were pooled and analyzed; the standard deviation is calculated from the analyses from the four replicate bottles for each treatment.

Hydroxylamine and hydroxyproline killed the plants. The other nitrogenous compounds were not toxic, and many of them supported rather good growth.

TABLE 2

Utilization of nitrogenous compounds by tomato plants grown under aseptic conditions

NITROGENOUS COMPOUND SUPPLIED*	EXPERIMENT 1		EXPERIMENT 2			
	Dry weight per plant relative to plants grown on ammonia†	Total N per plant relative to plants grown on ammonia†	Dry weight per plant and std. deviation of mean	Dry weight per plant relative to plants grown on ammonia†	Total N per plant and std. deviation of mean	Total N per plant relative to plants grown on ammonia†
			mgm		*mgm.*	
No added nitrogen	57	20	8.5 ± 0.17	84	0.151 ± 0.008	30
DL-α-alanine	71	74	13.6 ± 1.37	134	0.686 ± 0.034	134
β-alanine	78	89	8.4 ± 1.53	83	0.378 ± 0.086	74
α-amino-*n*-butyric acid	—	—	6.9 ± 0.15	68	0.260 ± 0.017	51
Ammonium sulfate	100	100	10.1 ± 1.19	100	0.513 ± 0.036	100
L-arginine	99	87	11.9 ± 0.52	118	0.578 ± 0.013	112
L-asparagine	69	67	11.8 ± 0.52	117	0.579 ± 0.014	112
DL-aspartic acid	100	88	11.9 ± 0.35	118	0.550 ± 0.051	107
Cysteine	—	—	11.7 ± 0.83	116	0.343 ± 0.010	67
L-cystine	95	71	12.6 ± 0.80	124	0.371 ± 0.025	72
DL-glutamic acid	101	74	17.5 ± 0.53	173	0.579 ± 0.016	112
L-glutamic acid	113	77	16.5 ± 0.87	163	0.576 ± 0.030	112
Glutamine	—	—	10.3 ± 0.25	102	0.542 ± 0.008	106
Glycine	112	101	13.5 ± 0.37	133	0.490 ± 0.006	95
L-histidine	111	81	14.2 ± 1.40	140	0.519 ± 0.017	101
DL-isoleucine	—	—	7.6 ± 0.68	74	0.233 ± 0.010	46
DL-leucine	65	51	10.8 ± 0.98	107	0.306 ± 0.033	60
L-leucine	103	67	9.3 ± 0.96	92	0.232 ± 0.018	45
L-lysine	88	67	12.4 ± 1.09	122	0.331 ± 0.015	65
DL-methionine	64	39	9.8 ± 0.93	97	0.281 ± 0.012	55
Nitrate, calcium	136	118	15.8 ± 1.44	156	0.518 ± 0.029	101
Nitrite, sodium	—	—	14.2 ± 1.69	140	0.621 ± 0.028	121
DL-norleucine	—	—	6.1 ± 1.25	60	0.220 ± 0.003	43
Oxime, α-keto-glutaric acid	—	—	10.3 ± 0.79	101	0.148 ± 0.017	29
Oxime, oxalacetic acid	—	—	8.4 ± 0.72	83	0.150 ± 0.032	29
Oxime, pyruvic acid	—	—	6.5 ± 0.65	64	0.137 ± 0.006	27
DL-phenylalanine	—	—	6.6 ± 0.58	65	0.214 ± 0.013	42
L-proline	—	—	11.4 ± 1.50	113	0.530 ± 0.034	103
DL-serine	—	—	5.9 ± 0.41	58	0.300 ± 0.032	59
DL-threonine	69	82	9.9 ± 1.67	98	0.384 ± 0.068	75
DL-tryptophane	—	—	7.0 ± 1.03	69	0.207 ± 0.020	40
L-tyrosine	—	—	7.0 ± 0.56	69	0.166 ± 0.012	32
DL-valine	—	—	6.7 ± 0.89	66	0.209 ± 0.006	41
Urea	—	—	12.4 ± 0.86	122	0.519 ± 0.015	101

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* John Baer variety tomato plants, five to a bottle, were supplied 3 mgm. N, as the compound listed, in 75 ml. of nutrient solution. Plants were harvested 6 weeks after planting.

† Plants grown on ammonium sulfate had 15.90 mgm. dry weight per plant and 0.631 mgm. total N per plant. Data for total N are not corrected for 0.043 mgm. N supplied by each seed.

The inorganic salts, ammonium sulfate, calcium nitrate, and sodium nitrite, effectively supplied nitrogen for growth. The best organic nitrogen sources were alanine, asparagine, arginine, aspartic acid, glutamic acid, glutamine, glycine, histidine, proline, and urea. Although hydroxylamine was detoxified by conversion to oximes, the oximes apparently were not assimilated, for the plants furnished oximes had less nitrogen than plants receiving no added nitrogen. The toxicity of hydroxyproline is interesting in view of its induction of abnormal growth in tobacco (15). Since with the tomato the variation between runs in the order of most suitable sources of organic nitrogen is almost as great as the variation between clover and tomato plants, it is concluded that although the two species of plants differ in their response to certain amino acids, their over-all response is reasonably similar.

Utilization of nitrogenous compounds by tobacco

Table 3 reveals that the inorganic sources of nitrogen, ammonia, nitrate, and nitrite, are far superior to any of the organic nitrogenous compounds. Not only does the tobacco plant use the organic compounds less effectively than do clover or tomato plants, but many more of the compounds inhibit the growth (but not nitrogen assimilation) of the tobacco plant compared to the control without added nitrogen. Alanine, arginine, asparagine, cysteine, glutamine, histidine, proline, and urea support reasonably good growth. The amides and urea can be considered as ready sources of ammonia. The mixture of amino acids and amino acids plus peptides represented by casein hydrolyzate and peptone supported fair growth, but less than that of several of the single amino acids and amides. Hydroxyproline suppressed all growth, as it did with tomato plants. The toxicity of aspartic acid was not observed, however, on plants other than tobacco.

Whereas clover and tomato utilized a variety of nitrogenous compounds in a rather similar manner, tobacco plants showed a strikingly different response from the other two species. Glutamic acid, aspartic acid, glycine, and the leucines were much poorer sources of nitrogen for tobacco than for the other plants tested.

Utilization of nitrogenous compounds by algae

The green alga *Chlorella pyrenoidosa* grown in liquid aerated culture did not utilize the following compounds: DL-methionine, L-lysine, DL-leucine, L-leucine, DL-norleucine, DL-glutamic acid, DL-serine, DL-threonine, DL-phenylalanine, hydroxylamine, and the oximes of α-ketoglutaric, oxalacetic, and pyruvic acids. Table 4 lists the percentage utilization of the nitrogen from the other compounds tested. The preference for ammonia and urea compared to nitrate is interesting as is the very poor utilization of nitrite. Hydroxyproline, which is toxic for tomato and tobacco plants, was about as effective as nitrate for the nutrition of the algae. Whereas α-alanine is a good source of nitrogen, β-alanine is used very poorly.

TABLE 3

Utilization of nitrogenous compounds by tobacco plants grown under aseptic conditions

NITROGENOUS COMPOUND SUPPLIED*	DRY WEIGHT PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†	TOTAL N PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†	NITROGENOUS COMPOUND SUPPLIED	DRY WEIGHT PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†	TOTAL N PER PLANT RELATIVE TO PLANTS GROWN ON AMMONIA†
No added nitrogen	8	3	Nitrate, calcium	136	106
DL-α-alanine	27	46	Nitrite, sodium	61	—
β-Alanine	3	7	DL-norleucine	6	4
Ammonium sulfate	100	100	Peptone	19	38
L-arginine	27	47	DL-phenylalanine	14	15
L-asparagine	31	49	L-proline	24	40
DL-aspartic acid	No growth	—	DL-serine	4	9
Casein hydrolyzate	19	33	DL-threonine	4	7
Cysteine	25	32	DL-tryptophane	5	4
L-cystine	14	20	L-tyrosine	12	17
DL-glutamic acid	11	18	DL-valine	4	5
L-glutamic acid	3	9	Urea	24	33
Glutamine	30	42			
Glycine	7	9			
L-histidine	26	36			
L-hydroxyproline	No growth	—			
DL-isoleucine	5	10			
DL-leucine	3	4			
L-leucine	4	4			
L-lysine	18	24			
DL-methionine	4	—			

* Comstock Spanish variety tobacco plants, five to a bottle, were supplied 3 mgm. N, as the compound listed, in 75 ml. of nutrient solution. Plants were harvested 6 weeks after planting.

† Plants grown on ammonium sulfate had a dry weight of 17.3 mgm. per plant and a total N content of 0.62 mgm. per plant. Data for total N are not corrected for 0.003 mgm. N supplied by each seed.

TABLE 4

Utilization of nitrogenous compounds by Chlorella pyrenoidosa

NITROGENOUS COMPOUND SUPPLIED	N ASSIMILATION RELATIVE TO AMMONIA*	NITROGENOUS COMPOUND SUPPLIED	N ASSIMILATION RELATIVE TO AMMONIA*
L-arginine	164.0	Nitrate, calcium	61.2
Glutamine	138.8	L-hydroxyproline	54.2
Cysteine	127.5	DL-aspartic acid	33.0
L-asparagine	108.4	Glycine	12.2
Ammonium sulfate	100.0	DL-valine	4.4
L-proline	77.4	α-amino-*n*-butyric acid	2.4
DL-α-alanine	75.5	β-alanine	1.6
Urea	72.8	Nitrite, sodium	0.9
L-glutamic acid	67.0	DL-tryptophane	0.9
DL-isoleucine	61.9	L-histidine	0.5

* The 50-ml. cultures on ammonia assimilated 4.4 mgm. N.

Utilization of nitrogenous compounds plus $N^{15}H_4^+$ by red clover

As certain amino acids are poorly utilized or are toxic, the question arises whether they will suppress the utilization of a good source of nitrogen, such as ammonia, when supplied together with it. Another question to be answered is whether, after initiation of substantial growth on a good source of nitrogen such as ammonia, the plant will use compounds which by themselves are poor sources of nitrogen. To investigate these points, plants were set up as described before, except that 2 mgm. of nitrogen as ammonium sulfate enriched with N^{15} and 2 mgm. of nitrogen as other compounds were placed in each bottle. Harvests were made at 4, 6, and 8 weeks, and the dry weight, total nitrogen per plant, and atom per cent N^{15} of the plants were determined. By using N^{15}-labeled ammonia, it is possible to find what fraction of the plant nitrogen originates from the ammonia supplied. The normal nitrogen comes from the seed, from traces of combined nitrogen contaminating the sand, or from the unlabeled nitrogenous compound furnished. In table 5 are recorded the dry weights and total nitrogen for the plants harvested at intervals and calculated values for the percentage nitrogen arising from ammonia, seed, or other compounds. The values for percentage nitrogen derived from each source are calculated in the following manner: The atom per cent N^{15} excess found is divided by 6.75 (atom per cent excess of ammonia supplied); this multiplied by 100 gives the percentage of the total nitrogen of the plant supplied by the ammonia. The assumption then is made that all of the nitrogen of the seed is assimilated by the plant, although this assumption is not entirely warranted, as is obvious from some of the data. As the average clover seed contained 0.091 mgm. nitrogen, 0.091 is divided by the total nitrogen per plant to find the percentage of the total nitrogen furnished by the seed. The sum of the percentage nitrogen from ammonia and the percentage nitrogen from the seed is subtracted from 100. This difference is attributed to nitrogenous compounds other than those supplied by the seed or as isotopically labeled ammonia. The value for percentage nitrogen from "other compounds," which includes contaminating nitrogenous compounds in the sand as well as the unlabeled compound supplied, is a *minimum* value, and the value for nitrogen derived from the seed is a *maximum* value. Although the calculated amounts of nitrogen from seed and "other compounds" are not absolute, they serve for comparative purposes.

The data show marked variability in dry weights but more uniformity in nitrogen assimilation by clover supplied a wide variety of nitrogenous compounds plus ammonia. This general level of nitrogen assimilation corresponds closely to that observed on ammonia alone. The results suggest that, given a choice of ammonia and an organic source of nitrogen, the plants use the ammonia in preference to the organic source of nitrogen, or, alternatively, that the presence of ammonia enhances the use of compounds poorly assimilated in its absence. Few of the amino acids inhibit the utilization of ammonia.

Although the ammonia supplied contained 6.75 atom per cent N^{15} excess, the plants furnished ammonia alone contained an average of 4.26 atom per cent N^{15} excess after 4 weeks. This indicates that the plants obtained about 37 per cent of their nitrogen from their seeds and contaminating compounds in the sand and 63 per cent from the ammonia supplied. All other plants had a choice of unlabeled nitrogen from their seeds and from an added nitrogenous compound plus isotopically labeled ammonia. None of these plants had as high N^{15} levels as had the control plants supplied with ammonia only; this indicated that they obtained a higher percentage of their nitrogen from the unlabeled sources than did the ammonia controls.

In general, the nitrogenous compounds previously shown to be most suitable for the nutrition of clover yielded plants with the lowest per cent N^{15} excess. Usually the concentration of N^{15} in the plants increased with time, and the percentage nitrogen derived from the seed was highest at the first harvest. This observation is interpreted to mean that the first nitrogen used by the plant is the nitrogen reserve in the seed, and when this is exhausted, the plant uses ammonia and builds up its N^{15} content. In some instances when the N^{15} level was high at the first harvest, it decreased at subsequent harvests (ammonia approaching exhaustion and other added nitrogenous compounds being used), whereas when it was low at the first harvest, it usually increased at later harvests (uptake of ammonia continuing actively). Another point of interest is that the inoculated plants had a high level of N^{15}. Apparently their fixation of nitrogen was suppressed by ammonia, and their nitrogen came chiefly from the seed and from ammonia.

The dry weights of plants grown on oximes were very high, but their assimilation of nitrogen was in the same range as that of plants on most of the other nitrogenous compounds. The consistent decrease in N^{15} with periodic harvesting suggests that oxime nitrogen was utilized. Even with a maximum allowance for nitrogen from the seed, a substantial utilization of oxime nitrogen still is indicated. During the relatively long period of the experiment, it is possible that the oximes decomposed to yield compounds other than hydroxylamine which were assimilated. Segal and Wilson (12) showed that hydroxylamine decomposes slowly to ammonia and other products which *Azotobacter vinelandii* can assimilate.

Although ammonia was used to supply a substantial part of the nitrogen for the clover plants under all conditions tested, nevertheless, all but a few of the other nitrogenous compounds supplied a share of the nitrogen to the plant in the presence of ammonia.

Utilization of nitrogenous compounds plus $N^{15}H_4^+$ by tobacco

Tobacco is somewhat more suitable than clover for testing the competition between ammonia and other nitrogenous compounds, for the reserve of nitrogen in the seed is smaller. Data from tests with tobacco are summarized in table 6. The following compounds were toxic or supported such poor growth that insufficient material for isotopic analysis was produced: α-amino-*n*-butyric acid, DL-aspartic acid, hydroxylamine, L-hydroxyproline, DL-methionine, and the oximes of α-ketoglutaric, oxalacetic, and pyruvic acids. When ammonium sulfate only was furnished, the plants had about 6 atom per cent N^{15} excess. Few of the

TABLE 5

Utilization of nitrogenous compounds plus $N^{15}H_4^+$ by red clover plants

NITROGENOUS COMPOUND SUPPLIED*	DRY WEIGHT PER PLANT			TOTAL N PER PLANT†			CALCULATED % TOTAL N DERIVED FROM NH$_4^+$‡			CALCULATED % TOTAL N DERIVED FROM SEED§			CALCULATED % TOTAL N DERIVED FROM OTHER COMPOUNDS		
	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*									
DL-α-alanine	5.2	7.8	7.9	0.18	0.33	0.27	28.5	35.5	37.8	50.5	27.6	33.7	21.1	37.0	28.5
β-alanine	3.2	7.2	9.3	0.18	0.31	0.33	—	24.6	37.2	50.6	29.4	27.6	—	46.0	35.2
α-amino-n-butyric acid	5.6	6.2	6.3	0.23	0.23	0.23	37.4	37.0	38.7	39.6	39.6	39.6	23.0	23.4	21.7
Ammonium sulfate, 2 mgm.¶	7.8	13.3	13.1	0.28	0.31	0.28	64.4	59.1	—	32.5	29.4	32.5	3.1	11.5	—
Ammonium sulfate, 4 mgm.¶	8.4	10.7	10.8	0.34	0.39	0.33	62.0	—	—	26.8	23.3	27.6	11.2	—	—
L-arginine	1.9	9.0	7.5	0.11	0.33	0.33	29.4	42.1	40.6	82.7‖	27.6	27.6	—	30.3	31.8
L-asparagine	3.4	5.5	—	0.18	0.27	—	31.4	37.7	—	50.5	33.7	—	18.1	28.6	—
DL-aspartic acid	4.2	8.2	8.8	0.22	0.23	0.28	36.6	41.7	41.8	41.3	39.5	32.5	22.1	18.8	25.7
Cysteine	1.5	5.2	4.4	0.09	0.19	0.18	24.8	39.4	42.2	100.0‖	47.8	50.5	—	12.8	7.3
L-cystine	2.2	8.3	—	0.11	0.27	—	31.2	45.2	—	82.8‖	33.8	—	—	21.0	—
DL-glutamic acid	4.6	7.8	9.3	0.21	0.34	0.42	36.3	45.5	43.5	43.3	26.8	21.7	20.4	27.7	24.8
L-glutamic acid	5.0	10.7	11.2	0.21	0.37	0.39	38.5	—	42.3	43.3	24.6	23.4	18.2	—	34.3
Glutamine	5.1	9.3	9.0	0.21	0.34	0.32	31.1	40.3	43.1	43.3	26.8	28.5	25.6	32.9	28.4
Glycine	1.2	3.0	10.3	0.07	0.21	0.38	26.8	37.0	36.0	100.0‖	43.3	24.0	—	19.7	40.0
L-histidine	2.6	5.2	7.8	0.13	0.25	0.32	31.1	34.4	41.9	70.0‖	36.4	28.5	—	29.2	29.6
L-hydroxyproline	2.3	1.8	—	0.11	0.09	—	28.2	31.6	—	83.0‖	100.0‖	—	—	—	—
Inoculated	5.9	8.4	13.0	0.26	0.34	0.47	51.1	58.0	47.4	35.0	26.8	19.4	13.9	15.2	33.2
DL-isoleucine	5.8	8.9	7.2	0.22	0.35	0.30	38.8	45.3	61.5	41.3	26.0	30.4	19.9	28.7	8.1
DL-leucine	4.7	6.3	4.7	0.22	0.27	0.19	37.8	37.5	—	41.3	33.8	48.0	20.9	28.7	—
L-leucine	5.0	5.8	6.2	0.21	0.25	0.29	37.5	36.0	43.4	43.3	36.5	31.4	19.2	27.5	25.2
L-lysine	1.4	1.0	—	0.07	0.05	—	31.6	31.6	—	100.0‖	100.0‖	—	—	—	—
DL-methionine	2.0	4.0	—	0.11	0.17	—	38.2	45.8	—	82.8‖	53.5	—	—	0.7	—
Nitrate, calcium	3.0	9.3	9.9	0.13	0.32	0.41	37.0	—	46.7	70.0‖	28.4	22.2	—	—	31.1
Nitrite, sodium	4.2	7.2	5.5	0.24	0.33	0.30	37.2	45.6	48.1	37.9	27.6	30.3	24.9	26.8	21.6
DL-norleucine	3.0	4.8	2.6	0.16	0.22	0.11	39.0	42.3	42.8	56.9	41.4	82.8‖	4.1	16.3	—

Oxime, α-ketoglutaric acid	7.7	13.9	16.1	0.31	0.39	0.34	56.0	51.4	29.8	29.4	23.3	26.8	14.6	25.3	43.4
Oxime, oxalacetic acid	6.9	13.7	14.8	0.29	0.34	0.33	60.5	54.1	51.5	31.4	26.8	27.6	8.1	19.1	20.9
Oxime, pyruvic acid	6.8	10.1	12.2	0.34	0.43	0.42	56.5	47.7	45.6	26.8	21.2	21.7	16.7	31.1	22.7
DL-phenylalanine	6.0	8.6	4.9	0.24	0.31	0.16	42.2	45.8	32.4	37.9	29.4	56.8	19.9	24.8	10.8
L-proline	6.7	12.4	15.8	0.27	0.51	0.55	50.7	39.0	51.0	33.7	17.8	16.6	15.6	43.2	32.4
DL-serine	5.3	7.7	8.8	0.21	0.28	0.30	37.0	—	37.5	43.4	32.5	31.3	19.6	—	31.2
DL-threonine	6.3	7.3	8.8	0.26	0.30	0.34	34.2	38.8	41.0	35.0	31.3	26.8	30.8	29.9	32.2
DL-tryptophane	5.2	11.8	5.6	0.23	—	0.23	43.1	—	47.1	39.6	—	39.6	17.3	—	13.3
L-tyrosine	5.5	6.1	8.4	0.22	0.24	0.27	44.8	45.5	45.1	41.3	37.9	33.7	13.9	16.6	21.2
DL-valine	4.8	6.5	8.1	0.22	0.31	0.35	37.2	34.7	42.5	41.3	29.9	26.0	21.5	35.9	31.5
Urea	6.4	8.6	8.5	0.29	0.37	0.23	29.0	26.3	34.5	31.4	24.6	39.6	39.6	39.1	25.9

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* Medium red clover plants, eight to a bottle, were supplied 2 mgm. N, as the compound listed, plus 2 mgm. N as ammonium sulfate containing 6.75 atom per cent N^{15} excess in 75 ml. of nutrient solution. Plants were harvested 4, 6, or 8 weeks after planting.

† Data for total N are not corrected for 0.091 mgm. N supplied by each seed.

‡ These values when multiplied by 0.0675 (atom per cent N^{15} excess in ammonium sulfate supplied divided by 100) give the atom per cent N^{15} excess in the plants harvested. The plants had from 1.66 to 4.34 atom per cent N^{15} excess.

§ For the purpose of calculation it is assumed that all of the nitrogen of the seed has been assimilated.

¶ Ammonium sulfate controls with 2 mgm. and 4 mgm. N were included.

‖ These data, based on the assumption of complete assimilation of the nitrogen of the seed, are obviously too high.

TABLE 6

Utilization of nitrogenous compounds plus $N^{15}H_4^+$ by tobacco plants

NITROGENOUS COMPOUND SUPPLIED*	DRY WEIGHT PER PLANT			TOTAL N PER PLANT†			CALCULATED % TOTAL N DERIVED FROM NH_4^+‡			CALCULATED % TOTAL N DERIVED FROM SEED§			CALCULATED % TOTAL N DERIVED FROM OTHER COMPOUNDS		
	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.	4 wks.	6 wks.	8 wks.
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*									
No added nitrogen	1.8	3.1	—	0.03	0.04	—	0.0	0.0	0.0	10.0	7.5	—	90.0	92.5	—
DL-α-alanine	1.0	2.6	17.3	0.09	0.18	0.70	48.6	38.6	39.1	3.3	1.7	0.4	48.1	59.7	60.5
β-alanine	0.4	5.0	14.8	0.03	0.29	0.58	52.8	43.7	55.3	10.0	1.0	0.5	37.2	55.3	57.1
Ammonium sulfate, 2 mgm.¶	2.4	7.7	14.1	0.11	0.41	0.60	86.7	90.9	88.8	2.7	0.7	0.5	11.6	8.4	10.7
Ammonium sulfate, 4 mgm.¶	2.3	9.0	15.8	0.14	0.30	0.44	93.2	86.7	79.3	2.1	1.0	0.7	4.7	12.3	20.0
L-arginine	1.6	4.5	7.7	0.12	0.34	0.37	48.1	39.0	45.5	2.5	0.9	0.8	49.4	60.1	53.7
L-asparagine	1.7	5.0	17.0	0.12	0.33	0.50	53.5	48.5	41.4	2.5	0.9	0.6	44.0	50.6	58.0
Casein hydrolyzate	2.7	7.3	17.1	0.17	0.32	0.48	45.7	41.0	44.5	1.8	0.9	0.6	52.5	58.1	54.9
Cysteine	0.6	4.6	15.4	0.04	0.20	0.56	48.5	54.4	53.3	7.5	1.5	0.5	44.0	44.1	45.2
DL-glutamic acid	0.3	0.6	1.8	0.04	0.07	0.19	43.4	—	44.2	7.5	4.3	1.6	49.1	—	54.2
L-glutamic acid	0.4	0.6	2.2	0.05	0.06	0.10	—	34.6	—	6.0	5.0	3.0	—	60.4	—
Glutamine	2.0	9.4	13.2	0.13	0.43	0.47	51.7	47.0	41.8	2.3	0.7	0.6	46.0	52.3	57.6
Glycine	0.5	7.2	6.5	0.06	0.39	0.49	48.1	39.7	43.3	5.0	0.8	0.6	46.9	59.5	56.1
L-histidine	0.6	1.0	—	0.04	0.12	—	38.1	42.4	—	7.5	2.5	—	54.4	55.1	—
DL-isoleucine	1.9	2.9	4.7	0.11	0.12	0.15	51.0	64.3	61.0	2.7	2.5	2.0	46.3	33.2	37.0
DL-leucine	1.1	3.4	15.5	0.08	0.20	0.51	50.3	—	54.4	3.8	1.5	0.6	45.9	—	45.0
L-leucine	2.4	9.3	11.8	0.17	0.34	0.39	44.6	45.0	52.3	1.8	0.9	0.8	53.6	54.1	46.9
L-lysine	1.2	5.1	11.3	0.06	0.23	0.33	62.3	53.8	58.2	5.0	1.3	0.9	32.7	44.9	40.9
Nitrate, calcium	2.7	12.8	19.8	0.15	0.56	0.68	52.9	46.5	44.8	2.0	0.5	0.4	45.1	53.0	54.8
Nitrite, sodium	5.3	13.4	23.0	0.21	0.69	0.79	52.9	44.3	40.0	1.4	0.4	0.4	45.7	55.3	59.6
DL-norleucine	1.3	3.5	3.7	0.04	0.22	0.10	55.7	57.5	59.8	7.5	1.3	3.0	36.8	41.2	37.2
Peptone	3.0	13.4	16.4	0.16	0.49	0.49	57.8	47.8	54.5	1.9	0.6	0.6	40.3	51.6	44.9
DL-phenylalanine	2.8	6.9	13.4	0.11	0.23	0.31	51.5	53.6	58.8	2.7	1.3	1.0	45.8	45.1	40.2
L-proline	2.6	11.0	19.0	0.18	0.49	0.59	43.9	52.9	50.1	1.7	0.6	0.5	54.4	46.5	49.4
DL-serine	2.0	8.6	11.3	0.13	0.37	0.45	43.9	46.4	45.1	2.3	0.8	0.7	53.8	52.8	54.2

DL-threonine	1.6	1.3	8.3	0.06	0.08	0.29	43.0	41.9	42.8	5.0	3.8	1.0	52.0	54.3	56.2
DL-tryptophan	1.2	3.4	1.9	0.05	0.12	0.08	51.6	51.0	—	6.0	2.5	3.8	42.4	46.5	—
L-tyrosine	2.7	8.8	9.3	0.11	0.25	0.25	65.0	60.0	67.3	2.7	1.2	1.2	32.3	38.8	31.5
DL-valine	1.5	7.1	8.9	0.11	0.28	0.29	50.3	52.7	55.4	2.7	1.1	1.0	47.0	46.2	43.6
Urea	1.1	6.2	17.0	0.08	0.27	0.54	47.4	46.5	45.9	3.8	1.1	0.6	48.8	52.4	53.5

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[*] Comstock Spanish variety tobacco plants, five to a bottle, were supplied 2 mgm. N, as the compound listed, plus 2 mgm. N as ammonium sulfate containing 6.75 atom per cent N^{15} excess in 75 ml. of nutrient solution. Plants were harvested 4, 6, or 8 weeks after planting.

[†] Data for total N are not corrected for 0.003 mgm. N supplied by each seed.

[‡] These values when multiplied by 0.0675 (atom per cent N^{15} excess in ammonium sulfate supplied divided by 100) give the atom per cent N^{15} excess in the plants harvested. The plants had from 2.57 to 6.29 atom per cent N^{15} excess.

[§] For the purpose of calculation it is assumed that all of the nitrogen of the seed has been assimilated.

[¶] Ammonium sulfate controls with 2 mgm. and 4 mgm. N were included.

other treatments (isoleucine, norleucine, tyrosine) yielded plants with over 4 atom per cent N^{15} excess. As the tobacco seed furnished very little nitrogen, it must be assumed that these low levels of N^{15} resulted from use of the nitrogen from the added organic nitrogenous compounds. The calculations summarized in table 6 indicate that usually one third to one half of the nitrogen came from the unlabeled nitrogenous compound supplied and about one half from the labeled ammonia furnished. Although, in general, ammonia appears to be superior to the other nitrogenous compounds, this superiority is not striking even at the first harvest. Frequently, however, plants from treatments with high level of N^{15} at the first harvest had lower levels at subsequent harvests.

TABLE 7

Effect of pyruvate on the utilization of nitrogenous compounds

COMPOUNDS SUPPLIED*	RED CLOVER		TOMATO		TOBACCO	
	Dry weight per plant	Total N per plant†	Dry weight per plant	Total N per plant†	Dry weight per plant	Total N per plant†
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
No added nitrogen	7.7	0.10			3.0	0.020
No added nitrogen + pyruvate	5.4	0.09			0.9	
Ammonium sulfate	8.5	0.27	10.2	0.51		
Ammonium sulfate + pyruvate	12.4	0.38	13.1	0.54		
Hydroxyproline	4.3	0.20			No growth	
Hydroxyproline + pyruvate	5.1	0.28			No growth	
Isoleucine	9.9	0.21	7.7	0.23	0.9	0.062
Isoleucine + pyruvate	6.4	0.25	7.6	0.31	0.4	0.021
Methionine		0.12				0.024
Methionine + pyruvate		0.10				0.030
Tryptophan		0.12				0.027
Tryptophan + pyruvate		0.11				0.037

* Plants were supplied 3 mgm. N, as the compound listed, plus or minus 0.214 millimoles sodium pyruvate in 75 ml. of nutrient solution. Plants were harvested 6 weeks after planting.

† Data for total nitrogen are not corrected for nitrogen furnished by the seeds.

Effect of pyruvic acid on utilization of nitrogenous compounds

Hutchinson and Miller (4) were unable to demonstrate any enhanced assimilation of ammonia when glucose was added to their aseptic cultures of peas. To determine whether the presence of an α-keto acid influences the utilization of nitrogenous compounds, plants were grown in the usual manner with 3 mgm. of nitrogen and with or without 0.214 millimoles of sodium pyruvate (equivalent to the nitrogen) supplied to each bottle. The results of the few tests made are summarized in table 7. The addition of pyruvate enhanced the growth of red clover and tomato on ammonia, although the amount of nitrogen taken up by the tomato plants was not increased appreciably. In absence of added nitrogen, the effect of pyruvate was inhibitory. It increased the growth and nitrogen assimilation of clover on hydroxyproline; and it inhibited growth of clover and tobacco, stimulated nitrogen assimilation by clover and tomato, and inhibited nitrogen assimilation by tobacco on isoleucine.

DISCUSSION

Unquestionably, clover and tomato plants can use a wide variety of organic nitrogenous compounds, and a marked similarity exists in their preferences for particular compounds. Tobacco is distinctly different in its preference for particular nitrogenous compounds and is much more sensitive to amino acids. Perhaps this difference is in part referable to the amount of reserve material in the seeds of tomato and clover compared with tobacco seeds. This also is suggested by the fact that certain of the amino acids, for example, glycine, β-alanine, DL-leucine, L-leucine, serine, threonine, and valine, which did not support good growth of tobacco (table 3) were used rather well when the plants were supplied ammonia in addition (table 6). Spoerl (14) observed that young orchid embryos, with virtually no reserve material, used only arginine among 19 amino acids tested, but older embryos could use aspartic acid also. The limited data permit no generalization, but apparently plants with seed reserves sufficient to get them well established use a greater variety of organic nitrogenous compounds than do plants with limited reserves.

Whereas inorganic nitrogen is much more effective than organic nitrogen for tobacco, certain organic compounds were found in some of our experiments to be superior to ammonia and nitrate for the nutrition of tomato and clover. This result suggests that direct assimilation of amino acids in soil under field conditions may be of importance in the nitrogen economy of plants. Vickery's (18) statement regarding the role of ammonia and nitrate appears rather extreme: "Few if any other forms of nitrogen can be utilized by the plant at all unless transformed into one or the other of these during the process of assimilation."

The question whether this direct assimilation of amino acids occurs in the presence of ammonia has been at least partly answered by the experiments with N^{15}-enriched ammonia. Isotopic analyses of plants grown in the presence of $N^{15}H_4^+$ and unlabeled amino acids are somewhat confused by the normal nitrogen supplied by the seed, but the results, in general, support the view: (*a*) in the earliest stages of growth the plant preferentially utilizes nitrogen from the seed; (*b*) as this reserve approaches exhaustion, the plant is dependent upon external sources of nitrogen and uses ammonia in preference to amino acids; (*c*) when the ammonia is depleted, the plant is forced to utilize the amino acids if it is to achieve further growth. Of course, there is no rigid division between these various stages; although the stages overlap, they seem broadly to represent the changes in the sources of nitrogen used by the plants.

It is recognized that the technique employed in these experiments is open to certain criticisms. The simple methods used were chosen to allow tests on a wide variety of substances, to remove the necessity for opening the culture bottles during the experiment, and to ensure conduct of the trials under bacteriologically controlled conditions. To achieve these objectives, we used methods that resulted in a restriction of nutrient and water supply and in time of growth. The considerable difference in the percentage nitrogen of plants from the various treatments suggests that all the amino acids absorbed may not have been readily assimilated but merely stored as such. If so, the data for dry weight as well as total nitrogen should be used as a measure of the effectiveness of the compounds. Another possible limitation or objection to the experiments is the restriction in the CO_2 supply to the plants. In a cotton-stoppered bottle the gas exchange may be so sluggish that CO_2, rather than the source of nitrogen, may limit the growth of the plants. This factor is more important as the plants become larger. The occasional stimulation induced by the addition of pyruvate suggests, for example, a possible limitation in the carbon supply.

Future work should probably concentrate upon intensive study of those compounds shown in this survey to be readily assimilated. In such studies attempts should be made to overcome the objections just discussed so as to grow plants to maturity under aseptic conditions. It would also be valuable to determine the relative use of ammonia (or nitrate) and various organic nitrogenous compounds in larger plants in which the influence of the nitrogen from the seed is minimized.

SUMMARY

Clover, tobacco, and tomato plants were grown aseptically to an age of 4 to 8 weeks on a variety of nitrogenous compounds. *Chlorella pyrenoidosa* also was tested for its ability to use these substances.

Clover and tomato showed considerable similarity in their response to organic nitrogenous compounds, and a number of amino acids supported excellent growth. Tobacco was much more sensitive to amino acids, and several inhibited the plant's growth. Organic nitrogen was not so effective as ammonia and nitrate in supporting growth of tobacco, but several amino acids supported more rapid growth of *Chlorella pyrenoidosa* than did nitrate and ammonia.

When ammonia labeled with N^{15} and a single amino acid were supplied together to tobacco and clover plants, all the cultures assimilated ammonia readily, but many of the amino acids also were used. Most of the amino acids that did not support good growth alone were not toxic, since plants supplied these amino acids plus ammonia grew rather well.

Analysis for the N^{15} content of clover and tobacco plants simultaneously furnished $N^{15}H_4^+$ and single amino acids indicated that usually the plant initially uses its reserve of seed nitrogen, then uses ammonia, and finally uses the nitrogen from the amino acids.

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EFFECT OF MATERIALS ABSORBED FROM THE ATMOSPHERE IN MAINTAINING SOIL FERTILITY

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Received for publication January 7, 1950

Despite the progress made in agricultural science in the last 100 years, much is still obscure even in regard to so fundamental a question as that of soil fertility. Fertility is commonly believed to be inherent in the soil, limited in amount, and subject to exhaustion by cropping. As the amount of plant food removed by a crop is easily measurable and as the composition of the soil itself is known, a simple calculation would suffice to determine how long present stocks of plant nutrients would last. If the nitrogen content of a given soil, for instance, is taken to be 0.1 per cent and total phosphorus 0.03 per cent, these two elements, which are generally the limiting factors in crop production, would be exhausted in little more than a single generation.

That this conclusion would be quite erroneous is shown by the classical long-term experiments at Rothamsted (6). The nitrogen content of the unmanured plot 3 (Broadbalk field), to a depth of 9 inches, was about 0.1 per cent in 1865, and it was still about 0.1 per cent in 1936 although in the interim 70 crops of wheat containing 2,100 pounds of nitrogen had been removed and an appreciable amount of nitrate (estimated at 15 pounds per acre per annum) had been lost in the drainage water. Obviously cropping has not exhausted the soil or even reduced appreciably its content of plant nutrients.

The same conclusion can be drawn from the fact that the natural vegetation of the South African veld or the prairies of America has persisted for thousands of years, giving sustenance to countless millions of large and small animals, and yet when the early settlers took possession they found, not a sterile desert, but a fruitful virgin soil.

Hall (3) reported that the Geescroft field at Rothamsted, unmanured and with no plants on it capable of fixing nitrogen, had gained in 20 years a considerable quantity of nitrogen, amounting to at least 25 pounds per acre per annum. Another example of the same kind is afforded by the redwood trees (Sequoia) of California, which not only have existed but have continued to grow for 2,000 or more years, without exhausting the soil or showing any sign of suffering from plant-food deficiencies.

All these examples point to the conclusion that some factor must be present by means of which actual additions of plant food are made continuously to the soil, replacing what has been removed by cropping and sufficient in absence of erosion to maintain fertility at a satisfactory level for an indefinite period.

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[1] Thanks are due to the chief, Division of Chemical Services of the Department of Agriculture, Pretoria, and to African Explosives and Chemical Industries, Natal, for facilities afforded in carrying out the experimental work on which this report is based.

A factor of this kind was believed to have been found in the fixation of nitrogen by microorganisms, but such a belief has proved illusory because the fixation of nitrogen depends on certain well-defined conditions which, outside the laboratory, are rarely fulfilled. One of these conditions is that the soil must be free from available nitrogen, since the presence of small quantities of ammonia or nitrate, for example, 10 ppm., is sufficient to inhibit fixation by the Azotobacter organism. Furthermore, fixation of nitrogen by microorganisms involves the destruction of 100 pounds organic matter (carbohydrates) for every pound of nitrogen fixed. In a very short time, therefore, the whole of the soil organic matter would be destroyed and further fixation would come to an end.

It is concluded, therefore, that nitrogen-fixing organisms contribute little to maintaining the nitrogen level of the soil. In any case, these organisms are not credited with being able to "fix" phosphorus, which is equally necessary and is even more liable than nitrogen to become exhausted in comparatively few years.

In search for the missing factor referred to above, attention was turned to a theory of Liebig's which has a bearing on the problem and which, although long ago discredited, is well worthy of re-examination. Liebig asserted that the nitrogen content of the soil was maintained by additions of ammonia in rain water and also as a result of adsorption from the air by the organic and inorganic colloids in the surface soil. The amount contributed by rain is about 5 pounds per acre in South Africa with a rainfall of 30 inches and may be as high as 12.8 pounds per acre in Ceylon with a rainfall of 110 inches. These amounts, although small, are definite and, in fact, offer a partial solution of the problem.

That the organic colloids consisting largely of cellulose may also play a part by adsorbing ammonia from the air is more difficult of proof. Because such organic matter already contains nitrogen which is subject to complex transformations in the soil due to the activities of ammonifying, nitrifying, nitrogen-fixing, and denitrifying organisms, it seems impossible to distinguish between the nitrogen obtained in these ways and that which might have been adsorbed from the air.

In the following experiments the difficulty was overcome by using at first pure cellulose, as typical of the soil organic matter, but treating it apart from the soil and in an air-dry condition. The amounts of ammonia, nitrate, and phosphoric oxide adsorbed from the air by pure, dry cellulose were determined by the methods of analysis given.

METHODS OF ANALYSIS

Ammonia nitrogen was determined by distillation with magnesia and nesslerization. After all ammonia had been distilled off, nitrate nitrogen was determined by addition of Devarda's alloy and by distillation and nesslerization as before. To determine the degree of accuracy to be expected in the estimation of small amounts of nitrogen, 13 different aliquots of a standard solution of NH_4Cl containing 10 ppm. nitrogen were distilled as above. The mean value of ammonia-N found was 9.5 ppm., standard deviation of mean 0.386, and standard error 0.107.

Phosphoric oxide was estimated colorimetrically by a modified Denigès method and the degree of accuracy determined from 10 different aliquots of a standard solution containing 10 ppm. of P_2O_5. The mean value found was 9.8 ppm., standard deviation 0.70, and standard error 0.22.

EXPERIMENTAL

A convenient form of pure cellulose for experiment was found in 12.5-cm. Whatman filter papers Nos. 41 and 50, which are described as acid-washed and which contain no nitrogen or soluble mineral matter. Before use these papers were washed in several changes of ammonia-free distilled water and then dried at room temperature. The dry papers were put in steel clips (three in a clip) and suspended in air, freely exposed to the breeze but protected from rain. After 1 to 7 days, the papers were again washed in several changes of ammonia-free distilled water and the washings distilled with magnesia until all ammonia had passed over into the receiver. The ammonia-N was determined by nesslerization and calculated as parts per million of the weight of the filter papers and also as milligrams per 1,000 sq. cm. of surface. The amounts adsorbed for 1, 2, 3, and 7 days respectively were as follows, the figures representing the mean of 10 experiments in each case:

	1 DAY	2 DAYS	3 DAYS	7 DAYS
NH_4-N adsorbed, ppm	35	52	64	94
NH_4-N adsorbed, mgm./sq. cm	0.15	0.23	0.28	0.41

The greatest amount was adsorbed in the first 24 hours, after which there was further adsorption but at a diminishing rate.

After use in these experiments, the same papers were dried and subjected to numerous further experiments of the same kind with approximately the same results.

It appears, therefore, that cellulose containing no nitrogen may nevertheless serve as a source of nitrogen to plants by alternately adsorbing ammonia from the air and transferring it to the soil by the agency of rain. Such "fixation" of nitrogen has nothing to do with microorganisms, which although doubtless present are unable to function under the conditions of the experiment.

The following experiments were devised to show the effect of various pH values on adsorption. Four sets of experiments A, B, C, and D were carried out at weekly intervals in the same way as before and determinations made of adsorbed ammonia, nitrate, and phosphoric oxide. In experiment A the papers were washed in ammonia-free distilled water only and then dried. In B the papers after being washed as before were finally rinsed in 0.01*N* HCl and dried. In C the same procedure was adopted, but the papers received a final wash in 0.01*N* Na_2CO_3 before being dried. In experiment D the same papers as in C were used again, but this time received a final wash in 0.01*N* HCl as in experiment B. The results were as follows (A, B, and C are the means of five weekly experiments):

	NH_4-N	NO_3-N	TOTAL N	P_2O_5
	ppm.	*ppm.*	*ppm.*	*ppm.*
A	31	9	40	2.8
B	113	13	126	2.5
C	9	13	22	2.0
D (1 experiment)	100	9	109	1.7

These results show that a slight increase in acidity, in B, resulted in a threefold increase of nitrogen adsorbed as compared with A and that a slight increase in alkalinity, in C, was followed by a drop to little more than half of the nitrogen adsorbed by A. Moreover, the ratio of NH_4-N to NO_3-N was reversed in C, NO_3-N exceeding NH_4-N.

Further experiments were carried out with cellulosic material of the kind present in crop residues and especially with those containing a high proportion of fiber relatively resistant to attack by soil organisms and, when air-dry, immune to such attack outside the soil. The fibrous material included dried grass, jute, sisal, and the woody fiber of sawdust or wood shavings. These were leached at weekly intervals with cold, ammonia-free distilled water and filtered, the mineral content of the filtrate being determined as before and calculated as parts per million on the original weight of the sample. The following figures represent the mean of four consecutive weekly experiments in each case:

	NH_4-N	NO_3-N	TOTAL N	CaO	P_2O_5
	ppm.	*ppm.*	*ppm.*	*ppm.*	*ppm.*
Dried grass	11	7	18	42	13
Jute fiber	84	19	103	103	10
Sisal fiber	51	20	71	70	5
Wood fiber	24	16	40	31	4
Filter paper	31	9	40	18	2.8

As these plant materials, although consisting chiefly of cellulose, contain some nitrogen, lime, and phosphoric oxide, it might be argued that these figures represent merely decomposition products. There was no decomposition under the conditions of this experiment, however, and the results of experiments A, B, C, and D show that pure cellulose can yield even higher figures for adsorbed nitrogen.

The leaves of trees consisting largely of cellulose act in the same way as the cellulosic materials represented by the dried grass and the jute, sisal, and wood fibers, that is, they adsorb from the air ammonia, nitrate, lime, and phosphoric oxide in the form of particles which are smaller than dust and which may be called "aerosols." Unlike the carbon in the atmosphere, these particles are not generally taken directly into the plant but, being water-soluble, are washed off the leaves by rain and enter the plant by way of the surface feeding roots. The amount of plant food received in this way is shown by the following experiment:

At 10 weekly intervals, a bunch of leaves of a nonleguminous evergreen tree, while still attached to the parent tree, was washed with cold ammonia-free distilled water. The solution was filtered and analyzed for water-soluble ammonia, nitrate, lime, and phosphoric oxide. Artificial "leaves" of pure cellulose consisting of Whatman filter papers torn in pieces and contained in a small wire cage suspended from the tree were treated in the same manner. The results, expressed as the means of the 10 weekly analyses in parts per million calculated on the weight of the leaves, were as follows:

	NH_4-N	NO_3-N	TOTAL N	CaO	P_2O_5
	ppm.	*ppm.*	*ppm.*	*ppm.*	*ppm.*
Leaves of tree	9	8	17	41	3.3
"Leaves" of cellulose....	19	5	24	18	1.7

The nitrogen in the washings from the leaves might be ascribed to an exudation from the substance of the leaf itself, but this explanation would not apply to the much greater amount of nitrogen from the artificial "leaves," which contained no nitrogen. The mineral matter adsorbed on the leaves is washed off by successive rains into the soil and may contribute to the growth of the tree indefinitely and independently of whatever other available plant foods may exist in the soil.

A better idea of the actual amount of plant nutrients gained in this way from a source outside the soil is given by the following experiment carried out at the seacoast of Natal.:

Rain water was collected in a rain gauge standing in the open and also, at the same time, in a jar that received the rain dripping from the leaves of a growing tree. Monthly determinations of the composition of the filtered rain water were made in each case separately, and the experiment was continued for 12 months, during which 49 inches of rain fell.

Results were as follows, the mean composition of the rain falling in the open and after dripping from the leaves of the tree being given as parts per million of rain and the total mineral matter, as pounds per acre per annum calculated from the total rainfall:

	RAIN	DRIP FROM TREE	
	ppm.	*ppm.*	*lb./A./yr.*
NH_4-N..................	0.86	2.6	28.6
NO_3-N...................	0.10	0.1	1.1
CaO......................	8.7	30.7	338
P_2O_5.....................	0.34	2.0	22

The amounts given in the last column are more than sufficient for the normal annual growth of forest trees. The surprisingly large amount of mineral salts is explained by the fact that the total area of the leaves, which are in many different planes and at varying heights from the ground, is much greater than the area of the base on which the tree stands. Actual measurements have shown that a maize plant 6 feet high may have a leaf area of 24 square feet, or more than 5 acres of leafage per acre of plants at the usual distance apart.

This experiment shows that trees can obtain from the air a large proportion of the nutrients they require and hence can live and grow for 100 or 1,000 years on the poorest soil, provided rainfall is adequate. Exactly the same conclusions are valid in regard to grass, which does not exhaust the soil but rather contributes to restoration of the fertility of eroded soil by adding to its carbon and nitrogen content.

DISCUSSION

The conclusion to be drawn from these experiments is that soil fertility is to be regarded, not as a static condition, but as a dynamic process taking place continuously at the surface of the soil and depending chiefly on the presence of cellulose or other organic colloids, which play the part of catalysts, alternately adsorbing ammonia and mineral matter from the air and transferring them in aqueous solution by the agency of rain to the roots of the growing crop. Fertility is thus a property, not of the soil as a whole, but of the colloids in the first inch or two of surface, which by virtue of the plus or minus electral charge on the surface layer are able to adsorb from the air, not only ammonia and nitrate but also lime, potash, phosphoric oxide, and other nutrients. These mineral particles probably exist in a form much finer than ordinary dust, for Blacktin (2, pp. 113, 138) mentions the existence in the air of particles having a diameter ranging from 10^{-5} to 10^{-7} cm. and described as aerosols which do not settle in a still atmosphere like the coarser dust particles and which, being almost infinitesimally small, are entirely water-soluble.

The importance of the surface soil to fertility was shown by Sreenivasan (7), who found that addition of 1 or 2 inches of surface soil taken from one plot and placed on top of an adjacent plot resulted in a crop increase of 80 per cent, and by Bennett (1, p. 215), who quotes data to show that, if the surface soil is removed by sheet erosion, yields may drop by 77 per cent or more.

Lebedjantzev (4) found that merely drying the surface soil under natural field conditions resulted in a large increase of fertility. A water extract gave an increase of 24 ppm. of ammonia and a twelvefold increase in water-soluble P_2O_5 above that from the undried soil. These experiments suggest comparison with the results of alternate wetting and drying of cellulose given in this paper. More recent experiments by Rossi (5) show that thin layers of soil exposed to the air "fix" an amount of nitrogen equivalent to 20 to 25 kgm. per hectare per annum. This effect was said to be independent of bacterial action and was renewed after each fall of rain.

The organic colloids in the surface soil include cellulose, lignin, and humus. According to microbiologists, cellulose can serve as energy material for nitrogen-fixing bacteria, but such fixation of nitrogen is accomplished at the expense of the organic matter, which is destroyed in the process and can therefore be used once only. On the other hand, cellulose used as a mulch in a dry condition at the surface of the soil is resistant to destruction by microorganisms and can adsorb from the air nitrogen compounds which are carried into the soil by successive rains. In this way, the same cellulose can function 100 or more times, exactly as the cellulose filter papers in the laboratory experiments previously described. These experiments throw light on the part played by humus in the maintenance of soil fertility. It is commonly assumed that humus contributes to fertility by undergoing decomposition, but Waksman (8, p. 115) has shown that humus, being in the form of a lignoprotein with a benzene nucleus, is highly resistant to decomposition by bacteria. Humus has, however, a high capacity for adsorbing ammonia especially at low pH values, but at pH greater than 6.5 this ammonia is readily lost. It is also pointed out that lignin and humus particles are negatively charged and that they adsorb ions containing elements which are of great importance in plant nutrition, for example, P, K, Ca, Mg, and Fe. Such adsorption quickly reaches a maximum, but if the elements adsorbed are leached into the soil by rain, further adsorption can then take place, and humus can in this way function almost indefinitely. Thus humus, acting as a catalyst, contributes nitrogen to the soil while its own stock of nitrogen, amounting to 4 or 5 per cent, remains intact.

According to the theory outlined above, there is no loss of fertility by cropping even after 70 years, as in the case already mentioned, and it is only when the surface soil itself is removed bodily, as in erosion, that there is any loss or deterioration. Thus fertility is not a wasting asset but a kind of capital which, though constantly expended, is as constantly replenished from the air in a never-ending cyclical process. The existence of epiphytes like certain tropical orchids which live on air and rain alone and yet have a composition similar to that of other orchids growing in the soil is a sufficient proof that air contains all the elements required for plant nutrition in adequate amounts and in a readily available form (not as insoluble dust).

If it is objected that the mineral content of the air is very small, being measured in parts per million, it is sufficient to point to the fact that the air is constantly in motion and that even in a gentle breeze more than a million cubic feet of air will come into contact with the growing plant every 24 hours. Even the carbon in the air amounts to only 160 mgm. per 1,000 liters, and yet this is sufficient to supply to annual crops a ton or more of carbon per acre. Another important consideration is that the mineral matter of the air is in the form of exceedingly fine particles (aerosols) which are completely water-soluble.

Although little has been said about the microorganisms of the soil, they nevertheless play an important part in any theory of fertility, not because they add anything to the soil, but because they break down the waste organic matter of crop residues and by resolving it into simpler compounds render it available as new building material for another generation of plants.

If plant nutrients are derived from the air, the question may be asked: Is the atmosphere an inexhaustible source of supply? The reply is that it is not, for according to estimates, even its carbon content, if not replenished, would be exhausted by growing vegetation in about 35 years. A complete theory of fertility therefore requires evidence of continuous additions to the air from some outside source of supply. Such a source is probably to be found in the ocean, which acts as a regulative device for maintaining more or less constant the carbon dioxide and ammonia content of the atmosphere. The mineral elements such as chlorine, calcium, and phosphorus which are found in rain water come probably from the sea as spray. Another source may be cosmic dust or terrestrial dust after it has been reduced to an extremely fine state of division. On this hypothesis, the fertility cycle would be from the sea to the air, from the air to the plant and the soil, and ultimately from the soil to the sea.

SUMMARY

Experiments have been described which show how cellulosic and related materials such as are found in plant residues and humus can adsorb, from the air, nitrogen and other compounds which are carried into the soil by successive rains and serve—in the absence of erosion—to maintain fertility at a moderate level for an indefinite period. For maximum crops, however, and especially of high-yielding and rapid-growing varieties, artificial fertilizers applied to the surface soil would still be required to supplement what is obtained from the air and soil.

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CHLOROPLAST PIGMENTS IN RELATION TO MAGNESIUM DEFICIENCY[1]

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Received for publication January 19, 1950

Since the classical researches of Willstäter and Stoll, it has been known that magnesium is the only metallic constituent of the chlorophyll molecule. It is also well known that a deficiency of this element in the soil results in a lower chlorophyll content of plant foliage, particularly of the older leaves. The effects of magnesium deficiency on the yellow pigments, carotene and xanthophyll, are not so well known. This paper reports part of the results of a study of magnesium deficiencies on different plants grown under field conditions.

A few studies have been made of the ratio of the chloroplast pigments in chlorotic and nonchlorotic leaves. Willstäter and Stoll (6) observed that the ratio of the green to yellow pigments in green leaves was remarkably constant. Oserkowsky (3) studied the ratio of the pigments in chlorotic and nonchlorotic pear leaves. Chlorosis in this case was due to growth of the pear trees in highly calcareous soil which induced iron deficiency. Normal leaves were taken from trees that had been sprayed with soluble iron salts. Carotene and xanthopyhll were determined together. The coefficient of correlation between chlorophyll and yellow pigments for 31 samples of chlorotic and nonchlorotic leaves were found to be 0.934. The ratio of chlorophyll to yellow pigments was higher in the nonchlorotic leaves than in the chlorotic ones. For eight samples described as "severely chlorotic" the ratio averaged 1.8; in nine "moderately chlorotic" samples it was 2.7; and in five samples of "green leaves from treated trees" it was 5.1. The smaller ratio for the chloritic leaves indicates a much greater deterioration of chlorophyll than of yellow pigments.

Mackinney (2) grew barley seedlings in nutrient solutions deficient in iron. The results indicated a close relation between chlorophyll and the carotinoids, but the ratio of carotene to xanthophyll was markedly lower in chlorotic leaves. No one heretofore seems to have made a study of the ratio of the three pigments when affected by magnesium deficiency under field conditions.

FIELD PLOTS USED

Plots at the Massachusetts Agricultural Experiment Station were used for the work. Two of the plots have received no magnesium for the last 50 years; two others received varying amounts from 1921 to 1935 and 150 pounds of magnesium sulfate per acre annually since 1935. One of the magnesium-treated plots and one of the magnesium-deficient plots received nondolomitic limestone in varying amounts from 1921 to 1935 and 1,000 pounds per acre annually since 1935. Since the latter date, all plots have received an annual per-acre application of 1,000 pounds of fertilizer compounded from sodium nitrate, potassium sulfate, and ammonium phosphate in proportion to give a 5-8-7 analysis.

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[1] Contribution No. 744, Massachusetts Agricultural Experiment Station, Amherst, Mass. Part of a thesis submitted by the senior author to the graduate faculty of the University of Massachusetts in partial fulfillment of the requirements for the degree doctor of philosophy. The senior author is greatly indebted to the International Minerals & Chemical Corporation for the financial support of this work under an industrial fellowship.

COLLECTION AND PREPARATION OF LEAF SAMPLES

It was frequently impossible to collect samples of the same species from all four of the field plots, since some plants failed to grow on the unlimed portion because of too high acidity (pH 4.6).

An attempt was made to take samples of leaves of approximately the same age on the plant. This was frequently difficult because of variation in growth and because of diseases that affected some plants more than others. Magnesium-deficient plots often had diseased plants, whereas the same species were virtually free from disease on the magnesium-treated plots.

TABLE 1

Effect of deep-freeze temperature (−20°C.) on chloroplast pigments

STORAGE PERIOD	CHLOROPHYLL	XANTHOPHYLL	CAROTENE
	Sugar maple leaves		
days	*mgm./gm.*	*mgm./gm.*	*mgm./gm.*
0	6.60	0.85	0.38
30	6.38	0.82	0.36
60	6.45	0.81	0.36
102	6.05	0.77	0.34
180	6.05	0.83	0.38
	Tobacco leaves		
0	11.35	1.47	0.68
30	11.08	1.40	0.60
60	11.60	1.38	0.58
102	11.40	1.34	0.58
180	11.30	1.42	0.66

All samples consisted of lower leaves, since these are affected most by magnesium deficiency. The samples were taken from the field plots at various times from June 5 to August 29, 1947. As little time as possible was allowed to elapse between the picking of the leaves and extraction of the pigments. This generally was not more than 1 hour. Usually a set of four samples was taken in the morning of one day and all analyses were finished by noon of the next. Precautions were taken to prevent as much loss of pigments by thermal and light decomposition as possible.

To determine whether any decomposition of pigments occurred during storage under deep-freeze conditions, sugar maple and tobacco leaves, picked during the latter part of August, were kept in a deep freezer at −20°C. for various periods up to approximately 6 months. The leaves were first cut into small pieces and those of each species thoroughly mixed. One set of samples was withdrawn and analyzed. Other sets were put in Mason fruit jars and placed in the deep freezer until analyzed. Table 1 gives the results of these analyses.

Tobacco and sugar maple were chosen because these two varieties of leaves represent about the extremes which one might expect in moisture content. Tobacco leaves are "wet" leaves, containing upwards of 90 per cent moisture when picked in the field. On the other hand, sugar maple leaves represent a "dry" type, usually having only about 45 to 50 per cent moisture. It was thought that the amount of moisture might affect the keeping quality of the leaves under deep-freeze conditions. The results in table 1 show, however, that moisture was not a factor in the keeping quality of the leaves and that very little decomposition of the pigments occurred during the storage period.

METHOD OF PIGMENT ANALYSIS

Chlorophyll was extracted from the fresh plant leaves and determined by the Petering-Wolman-Hibbard method (4). A Klett-Summerson glass cell industrial model photoelectric colorimeter, which was calibrated for chlorophyll by the method of Comar, Benne, and Buteyn (1), was used.

Carotene was determined on a 50-ml. aliquot of the original acetone extract. Chlorophyll was removed by absorption on finely divided barium hydroxide according to a method described by Petering, Wolman, and Morgal (5). Xanthophyll was removed by phasic separation with methanol in the usual manner. The colorimeter was calibrated by using light filter No. 44 against a known solution of pure beta carotene in petroleum ether.

Xanthophyll was determined on the methanol extracts by using the same light filter and the same calibration curve used for carotene.

All pigment results are expressed as milligrams per gram of oven-dried plant tissue. The aliquot of the plant material used to determine the dry weight was dried overnight in a steam oven at 60° to 70°C. and then placed in an electric oven at 100°C. for another overnight period.

RESULTS

Table 2 shows the chlorophyll, xanthophyll, and carotene contents of leaves from 13 different plants grown on the unlimed plots. Table 3 presents similar data for 18 different plants grown on the limed plots.

Chemical analysis[2] of plants gown in the magnesium-deficient soil that had been limed indicated a decrease in the amount of magnesium absorbed. Several theories have been advanced to explain this phenomenon, such as preferential ion absorption or ion antagonism. In view of this, it was expected to find a greater loss of chlorophyll, xanthophyll, and carotene in plants grown on the magnesium-deficient limed plots. The data presented in table 4 do not warrant any clear-cut

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[2] Data not presented in this paper.

TABLE 2

Effect of magnesium deficiency on chloroplast pigments of plants grown in unlimed plots

In milligrams per gram oven-dried plant tissue

PLANT	CHLOROPHYLL		XANTHOPHYLL		CAROTENE	
	Plot A, no Mg added	Plot B, Mg* added	Plot A, no Mg added	Plot B, Mg* added	Plot A, no Mg added	Plot B, Mg* added
Apple	5.49	4.54	0.57	0.55	0.29	0.28
Eggplant	2.47	8.24	0.55	0.94	0.30	0.44
Hibiscus	4.19	9.50	0.24	1.20	0.28	0.50
Marigold	11.93	10.64	1.54	1.44	0.28	0.22
Meadow rue	1.84	6.70	0.31	1.01	0.18	0.34
Mock orange	6.26	8.54	0.89	1.10	0.27	0.42
Oak	8.05	5.45	1.03	0.75	0.38	0.29
Petunia	7.43	9.83	0.96	1.27	0.31	0.42
Raspberry	5.48	8.10	0.43	0.56	0.17	0.22
Snapdragon	6.81	9.27	0.82	1.14	0.28	0.43
Sweet corn	4.68	10.45	0.59	1.23	0.32	0.71
Thunbergia	5.92	6.64	0.81	0.90	0.33	0.37
Tobacco	3.40	8.43	0.61	1.04	0.28	0.57
Tomato	2.04	12.20	0.39	1.33	0.30	0.73

* 150 pounds $MgSO_4 \cdot 7H_2O$ per acre.

TABLE 3

Effect of magnesium deficiency on chloroplast pigments of plants grown in limed plots

In milligrams per gram oven-dried plant tissue

PLANT	CHLOROPHYLL		XANTHOPHYLL		CAROTENE	
	Plot A, no Mg added	Plot C*, Mg added	Plot A, no Mg added	Plot C*, Mg added	Plot A, no Mg added	Plot C*, Mg added
Apple	4.40	4.55	0.54	0.51	0.27	0.21
Bush honeysuckle	2.77	8.20	0.44	0.96	0.18	0.54
Carrot	3.16	8.45	0.53	1.05	0.23	0.53
Eggplant	3.65	7.86	0.60	0.80	0.24	0.41
Hibiscus	4.04	7.10	0.31	1.02	0.26	0.46
Lavatera	6.04	16.42	0.89	2.06	0.34	0.83
Marigold	6.77	8.60	0.92	1.24	0.15	0.20
Oak	5.33	4.57	0.62	0.63	0.28	0.24
Pepper	11.53	12.23	1.30	1.18	0.49	0.44
Petunia	4.28	9.95	0.66	1.16	0.20	0.45
Raspberry	3.84	7.64	0.23	0.54	0.08	0.24
Snapdragon	8.80	9.43	1.20	1.28	0.43	0.45
Sunflower	10.51	10.62	1.28	1.12	0.55	0.52
Sweet corn	7.51	10.76	0.86	1.25	0.50	0.74
Tobacco	3.30	8.50	0.50	0.98	0.23	0.50
Tomato	4.42	9.86	0.58	1.02	0.28	0.51
Thunbergia	5.95	8.05	0.73	1.03	0.31	0.39
Zinnia	5.36	7.56	0.65	0.87	0.31	0.43

* 150 pounds $MgSO_4 \cdot 7H_2O$ per acre.

decision in this matter. Some of the plants have a greater loss of chlorophyl on the unlimed plots; others have greater loss on the limed plots.

Regression studies were made of the relationship of the three pigments. The data in table 4 were grouped together for both the limed and the unlimed plots. Figure 1 gives the regression of xanthophyll losses upon the chlorophyll losses in the plant leaves grown on magnesium-deficient plots, irrespective of whether the plots were limed or unlimed; figure 2 gives the regression of carotene losses upon the chlorophyll losses; and figure 3 gives the regression of xanthophyll losses upon the carotene losses. Positive coefficients of correlations were obtained in all cases. This would indicate that magnesium deficiency affects not only the chlorophyll content of plant leaves but the carotene and xanthophyll as well. The regression studies indicated that with the loss of each part of carotene, twenty parts of chlorophyll were lost. Also, the loss of each part of xanthophyll was accompanied by a loss of ten parts of chlorophyll. These relationships would indicate that there is an association of the three pigments in the chloroplast in a ratio of twenty parts of chlorophyll to two parts of xanthophyll to one of carotene. Apparently these relationships are not appreciably disturbed by magnesium deficiency, and the three pigments are lost in proportional amounts.

TABLE 4

Loss of leaf pigments due to magnesium deficiency of plants grown on limed and unlimed plots
In milligrams per gram oven-dried plant tissue

PLANT	CHLOROPHYLL		XANTHOPHYLL		CAROTENE	
	Unlimed plots	Limed plots	Unlimed plots	Limed plots	Unlimed plots	Limed plots
Bush honeysuckle......	—	5.43	—	0.52	—	0.36
Carrot..................	—	5.29	—	0.52	—	0.30
Eggplant..............	5.77	4.21	0.39	0.20	0.14	0.17
Hibiscus...............	5.31	3.06	0.96	0.71	0.22	0.20
Lavatera..............	—	10.38	—	1.17	—	0.49
Marigold..............	—	1.83	—	0.32	—	0.05
Meadow rue...........	4.86	—	0.70	—	0.16	—
Mock orange...........	2.28	—	0.21	—	0.15	—
Petunia................	2.40	5.67	0.31	0.50	0.11	0.25
Raspberry.............	2.62	3.80	0.13	0.31	0.05	0.16
Snapdragon.............	2.46	0.63	0.32	0.08	0.15	0.02
Sweet corn............	5.77	3.25	0.64	0.39	0.39	0.24
Thunbergia............	0.72	2.10	0.09	0.30	0.04	0.08
Tobacco................	5.03	5.20	0.43	0.48	0.29	0.27
Tomato................	10.16	5.44	0.94	0.44	0.43	0.23
Zinnia..................	—	2.20	—	0.22	—	0.12

Others who have investigated various phases of pigment relationships in plants have laid considerable stress on certain ratios between the various pigments. Pigment ratios calculated for the plants grown on magnesium-deficient plots and on magnesium-treated plots are given in table 5.

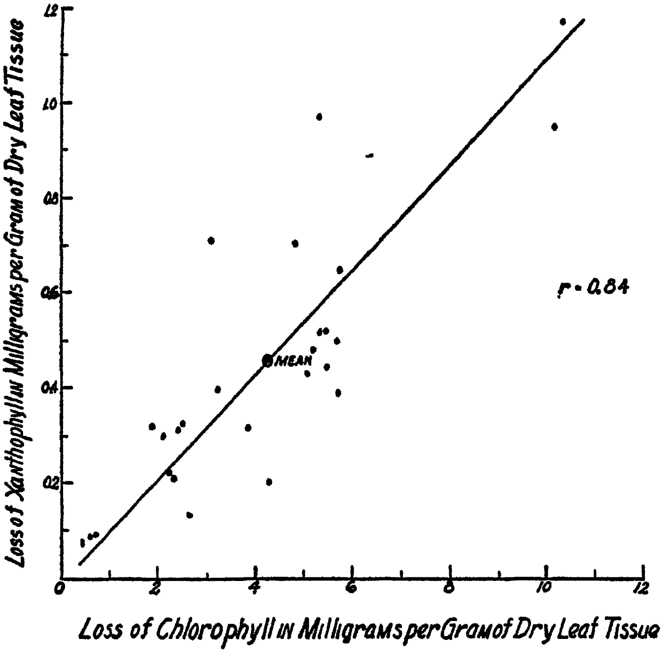

FIG. 1. REGRESSION OF XANTHOPHYLL LOSSES ON CHLOROPHYLL LOSSES

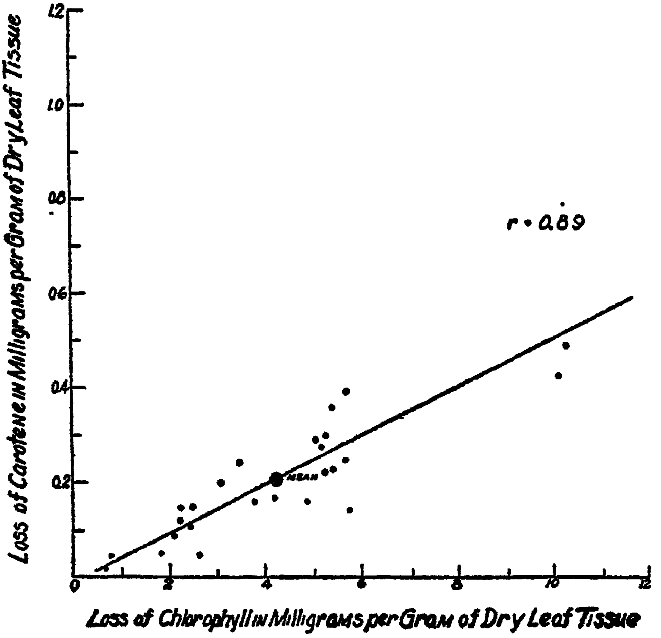

FIG. 2. REGRESSION OF CAROTENE LOSSES ON CHLOROPHYLL LOSSES

Since the ratios are virtually the same whether they are calculated from samples taken from the magnesium-deficient plots or from the magnesium-treated plots, the only conclusion that can be drawn is that a deficiency of magnesium does not disturb the proportions of the various pigments one to another. In other words, the ratios are the same in chlorotic and nonchlorotic leaves. In this respect, magnesium deficiency apparently differs from iron deficiency.

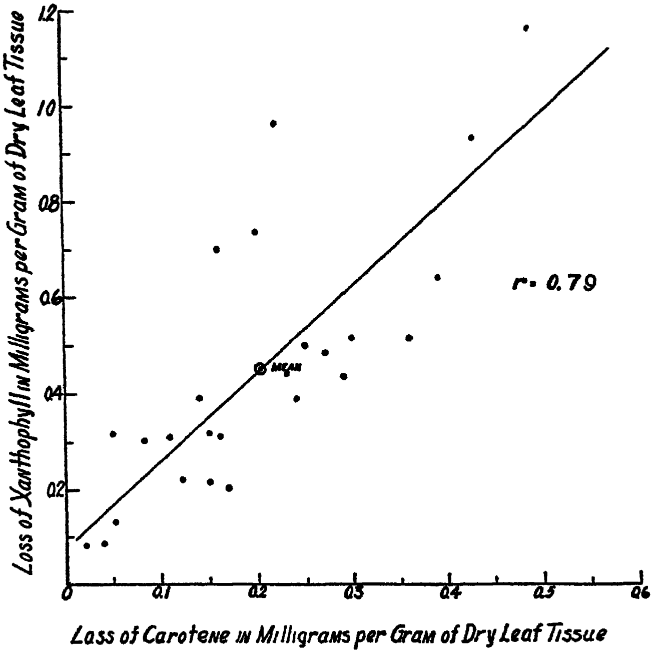

FIG. 3. REGRESSION OF XANTHOPHYLL LOSSES ON CAROTENE LOSSES

TABLE 5

Effect of deficiency of magnesium on average pigment ratios

RATIOS	MAGNESIUM DEFICIENT PLOTS	MAGNESIUM-TREATED PLOTS
Chlorophyll:xanthophyll	8.25	8.56
Chlorophyll:carotene	20.80	19.43
Xanthophyll:carotene	2.58	2.80
Chlorophyll:carotinoids	5.72	5.85

SUMMARY

A study of the effect of magnesium deficiency upon the chlorophyll, xanthophyll, and carotene content of leaves of different plants indicated that magnesium deficiency causes not only a loss of chlorophyll in the lower leaves, but also a loss of xanthophyll and carotene. The loss of each twenty parts of chlorophyll was accompanied by a loss of two parts of xanthophyll and one part of carotene.

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A PEDOLOGIC STUDY OF A PODZOL SOIL PROFILE FROM THE EQUATORIAL REGION OF COLOMBIA, SOUTH AMERICA

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Received for publication January 3, 1950

One of the interesting aspects of the soil study of the equatorial regions of Colombia, South America, reported by Jenny (13) was the disclosure of the presence of podzols. Although podzols or podzolized soils were reported previously in the equatorial regions, their podzolized character was established mainly by their gross morphological features (26).

To resolve any doubts as to the true podzol character of such equatorial soils, the profile described by Jenny as a "giant podzol" (13, table 5) was thoroughly investigated. The results of this investigation are reported in tables 2–10, and figures 4–7. The site of the profile and a close-up view of another shallower podzol profile are shown in figures 1 and 2. A brief description of the profile is given in table 1.

In gross morphological features the similarity of this profile to a podzol lies mainly in the presence of a bleached horizon (layers *c* and *d*) and a very marked horizon of iron accumulation (layer *e*)—an ortstein layer—both of which are parallel to the surface. The profile, however, differs from an ordinary podzol in, first, the presence of a very thick mineral horizon—the A_1—rich in organic matter above the bleached horizon; second, the giant dimensions of the A_1 and A_2 horizons; and third, the extremely large accumulation of Fe_2O_3 in the B_1 horizon.

DISCUSSION OF RESULTS

The unusual features of the profile suggest that it would be advisable to establish the nature and uniformity of the parent material before proceeding with a discussion of the podzol properties of the profile.

Nature of the parent material

The differential thermal analyses of the whole soil and of various particle-size fractions (figs. 4–) are perhaps the clearest evidence of the stratified nature of the profile. These analyses show the presence of large amounts of kaolinitic material in the *f* and *g* layers, but none in the *a*, *b*, *c*, and *d* layers. The mineralogical analyses of the whole soil (table 4) also support this conclusion. This is clearly shown by both the heavy and the light minerals. The *a*, *b*, *c*, and *d* layers contain a certain amount of hornblende and biotite, whereas the *f* horizon contains only a trace or none. The mineralogical composition of the light minerals

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[1] Ministerio de Minas y Petroleos, Bogotá. The writers are indebted to H. Jenny for collecting the profile, for supplying figures 1 and 2, and for his constructive suggestions and criticism of this manuscript.

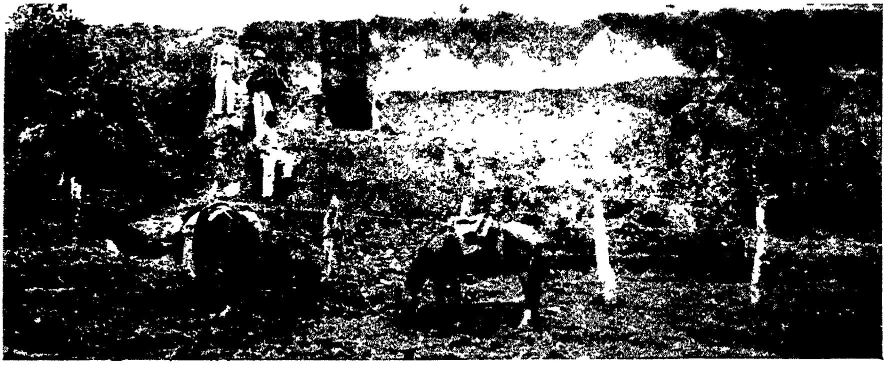

Fig. 1. The Sabaneta Profile, Showing the Giant Dimension and General Appearance

The site is a road-cut near Albán between Bogotá and Onda.

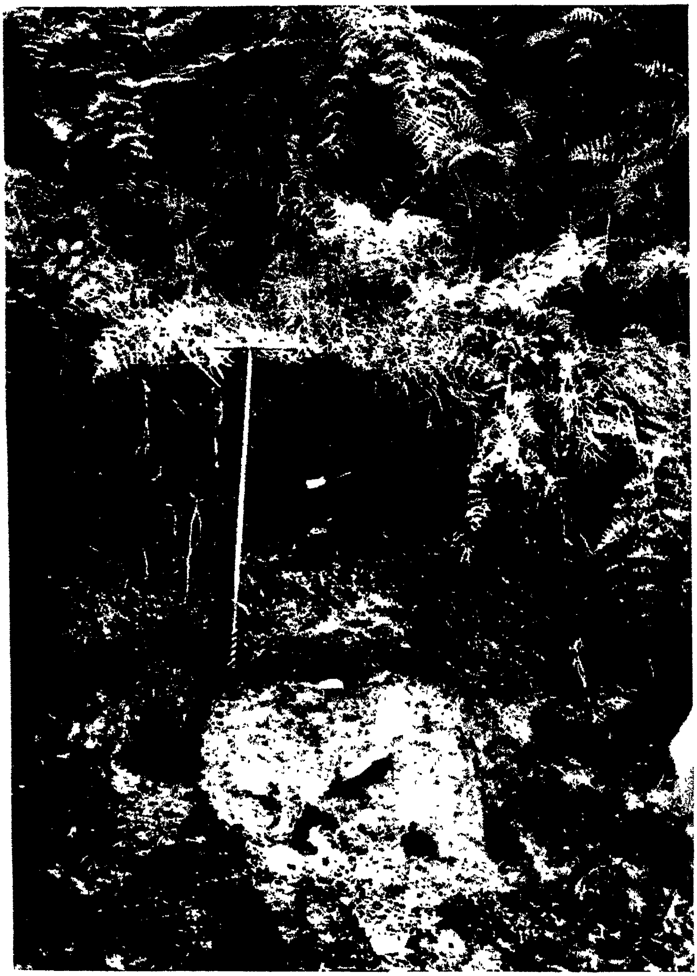

Fig. 2. A Sabaneta Profile Similar to That From Albán but of Smaller Dimension

and the mechanical analysis show that the *a*, *b*, *c*, and *d* layers are high in quartz and volcanic glass and low in clay, whereas the *f* layer is relatively low in quartz and high in clay and contains no volcanic glass.

It is very difficult to conceive of pedologic processes which would alter a material of the nature of the *f* or *g* layers to soil material of the nature of the *a*, *b*, *c*, and *d* layers. One must conclude, therefore, that the parent material of this profile was stratified.

TABLE 1

Giant podzol

Sabaneta series, No. 94

Locality: near Albán (Cundinamarca, about 5°N), elevation 2460 m. (8,070 feet).
Climate: estimated, temperature 17°C. (63°F.), precipitation 2,000 mm. (79 inches).
Vegetation: now pasture, originally forest with a dense cover of ferns (see fig. 2).
Topography: gently sloping fan, slope 5–10 per cent.
Parent material: semiconsolidated crystal tuff (*a*, *b*, *c*, *d*, and *e* layers) underlain by a kaolinitic shale (*f* and *g* layers) (see table 4).
Profile description:

DEPTH	LAYER DESIGNATION	HORIZON DIFFERENTIATION	COLOR
inches			
−2–0		A_0	Humus layer, black very soft (19, 28)*
0–18	*a*	A_1	Grayish brown, 10 YR 4/2†, moderately cloddy, of high friability and high permeability to water, air, and roots
18–32	*b*		Pale brown, 10 YR 6/3, otherwise similar to *a*
32–45	*c*	A_2	Light gray, 2.5 Y 7/2, moderately bleached, moderately cloddy, of medium friability, and high permeability
45–56	*d*		White, 2.5 Y 8/3, strongly bleached, otherwise similar to *c*
56–60	*e*	B_1	Yellowish red, 5 YR 5/8, laminated with iron oxide and full of iron concretions, of low friability and with low permeability to water, air, and roots. An ortstein horizon
60–80	*f*	B_2	Yellow, 10 YR 8/6, of medium friability and with fairly good drainage
80+	*g*		Hard kaolinitic shaly rock

* Absent in this profile but present in the virgin profile (fig. 2).

† The color specifications correspond to the Munsell notations.

The stratification of the parent material, however, does not exclude the possibility that the ortstein horizon (the *e* layer) was formed by the accumulation of iron from the overlying horizons. The probability that the ortstein horizon is of genetic origin would be enhanced if it could be shown that the parent material of this layer was more like the parent material of the overlying horizons than that of the underlying horizons. A careful study was therefore made of the ortstein layer. It was noted that the sand fractions from this horizon consisted of three distinct types of particles; namely, rust colored, rose colored, and yellow colored. A differential thermal curve was run on each (fig. 7). Differential thermal curves were also made of the whole sand and the silt fractions (figs. 6 and 7). A comparison of these curves, in the region between 450° and 550° C. and in the region of 900°C. with those of the fractions from the overlying and underlying horizons and with the differential thermal curves of bauxite and kaolinite (fig. 7) shows the following: 1. The differential thermal curve of kaolinite differs from that of bauxite mainly in having an exothermic break at about 900°C. The absence or near absence, therefore, of an exothermic break at 900°C

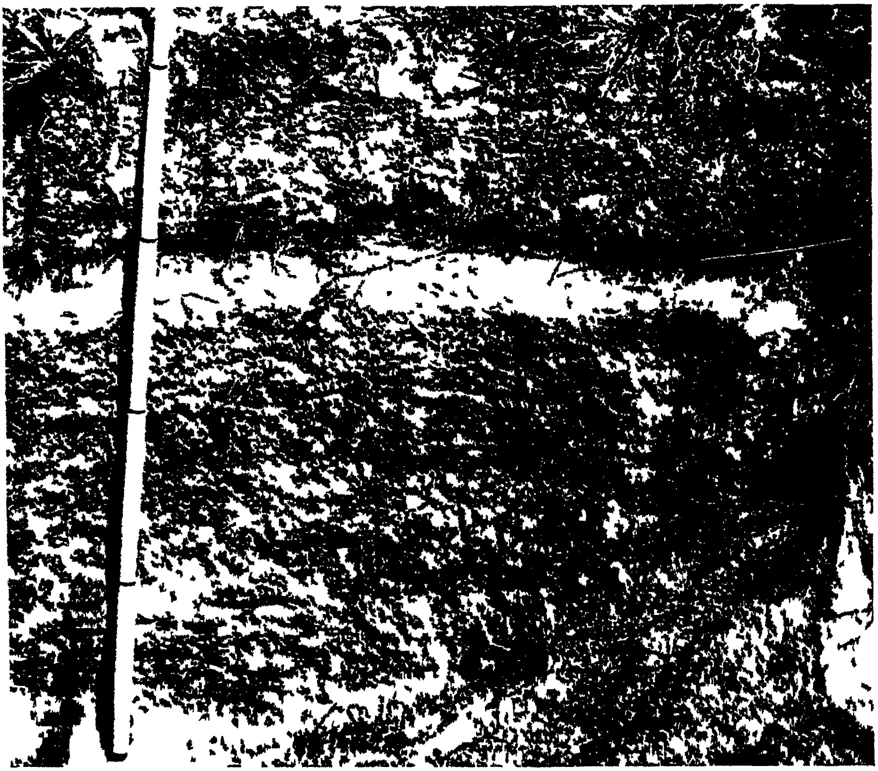

Fig. 3. A Podzol Profile under Grass Vegetation from the High Sierra Nevada Mountains of California—Elevation 10 000 Feet

in the differential thermal curves of the rust, the rose, the whole sand, and the silt fractions indicates that kaolinite is nearly absent in these fractions, and the endothermic break in the region from 450° to 550°C. indicates the presence of bauxite rather than kaolinite. 2. The yellow particles contain some kaolinite and therefore are similar in this respect to material from the underlying horizon. The amount of this material in the whole soil is very small, however, as shown by the very small exothermic break at 890°C. in the differential thermal curve of the whole soil, the sand, or the silt fraction. Perhaps these particles represent contamination of the B_1 sample with some of the material from the B_2 horizon during sampling.

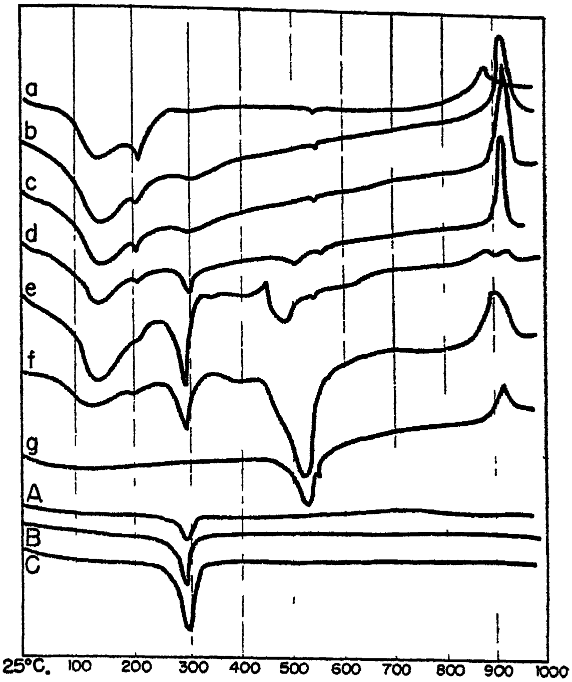

FIG. 4. DIFFERENTIAL THERMAL CURVES: *a, b, c, d, e, f,* AND *g* OF THE WHOLE SOIL, Ca-SATURATED AND FREE FROM ORGANIC MATTER, FROM THE *a, b, c, d, e, f,* AND *g* LAYERS RESPECTIVELY; A = 2 PER CENT GIBBSITE AND 98 PER CENT IGNITED Al_2O_3; B = 5 PER CENT GIBBSITE AND 95 PER CENT IGNITED Al_2O_3; C = 7 PER CENT GIBBSITE AND 93 PER CENT IGNITED Al_2O_3.

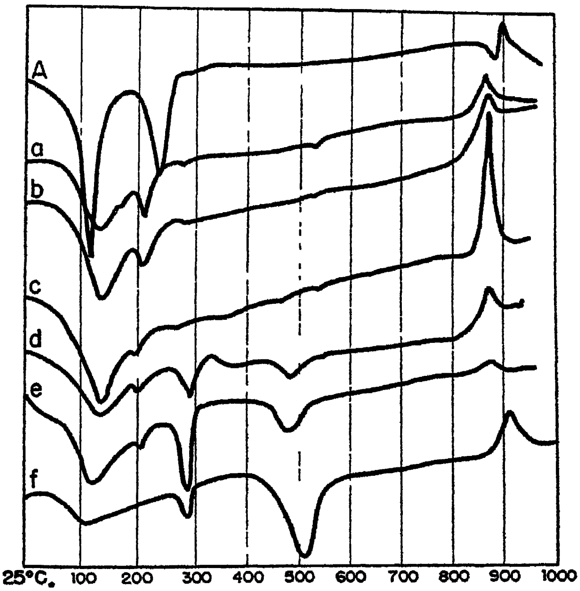

FIG. 5. DIFFERENTIAL THERMAL CURVES: *a, b, c, d, e,* AND *f* OF THE <1 μ CLAY, Ca-SATURATED AND FREE FROM ORGANIC MATTER, FROM THE *a, b, c, d, e,* AND *f* LAYERS

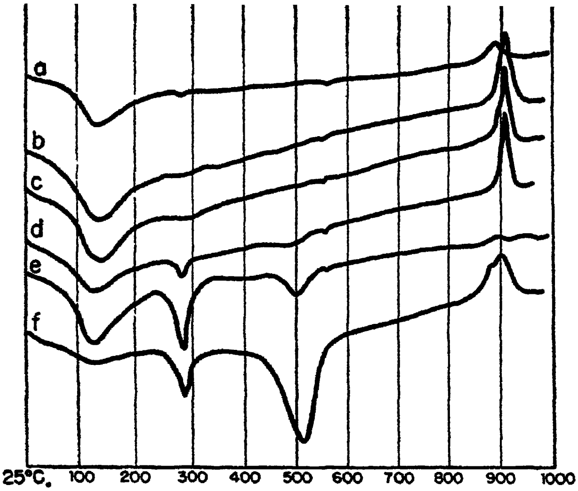

Fig. 6. Differential Thermal Curves: *a*, *b*, *c*, *d*, *e*, and *f* of the silt Fraction (0.05–0.005mm.), with the Natural Base Status and Free from Organic Matter, from the *a*, *b*, *c*, *d*, *e*, and *f* Layers Respectively.

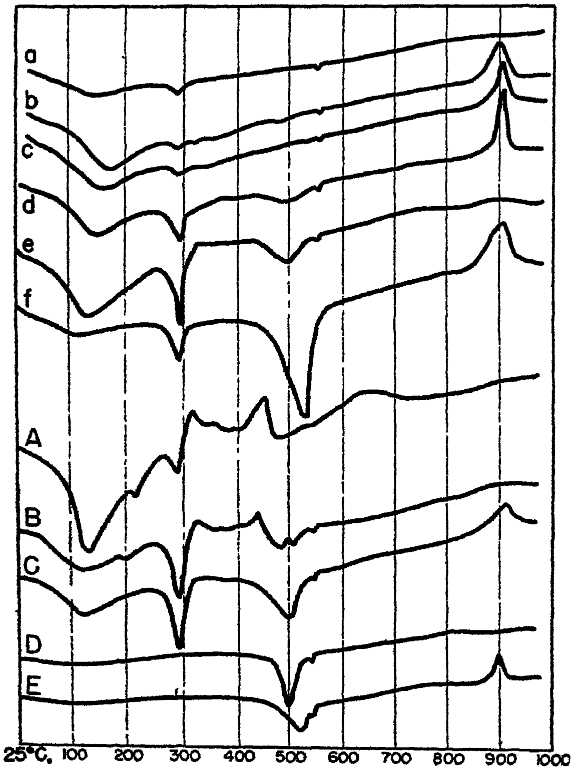

Fig. 7. Differential Thermal Curves: *a*, *b*, *c*, *d*, *e*, and *f* of the Sand Fractions (2.0-0.05 mm.), with the Natural Base Status and Free from Organic Matter, from the *a*, *b*, *c*, *d*, *e*, and *f* Layers Respectively; A, B, C, = Rust, Rose, and Yellow Sand Fractions Respectively from the *e* Layer; D = 10 per cent Bauxite (from Beaux,

The near absence of kaolinite in the ortstein layer indicates that the parent material of this layer was not of the same kind as the underlying material. On the other hand, a comparison of the chemical composition of the material from the various horizons based on the absence of Fe_2O_3, Al_2O_3, and volatile matter (organic matter and H_2O), the main substances which have been moved or accumulated in the profile, shows that the CaO, MgO, and Na_2O contents of the *e* layer (the ortstein horizon) are similar in magnitude to those of the overlying layers rather than to those of the underlying *f* layer (table 7). This similarity of the *e* layer to the overlying layers is particularly significant, since the amounts of CaO, MgO, and Na_2O are considerably smaller in the *f* layer than in the overlying layers, a condition not encountered in strongly weathered soils developed from uniform parent material. The similarity of the *e* layer to the overlying layers is also brought out very clearly by, first, the base-exchange capacity of the iron– and organic-matter–free clay from the *e* layer and of the clays from the *a*, *b*, *c*, and *d* layers (table 9), and second, the mineralogical composition of the whole soil (table 4). These results indicate that the parent material of the *e* layer was undoubtedly identical to that of the *a*, *b*, *c*, and *d* layers. This conclusion together with the fact that the ortstein layer is only 4 inches thick and contains a large amount of organic matter makes it appear more probable, therefore, that the orstein layer is of a genetic origin. Although most of the Fe_2O_3 accumulated in the *e* horizon, a little was also deposited in the *f* layer as shown by the free Fe_2O_3 (table 4). The distribution of gibbsite in the profile (fig. 4) indicates that the *f* layer was also a recipient of a little gibbsite. The presence of gibbsite in the *f* layer but not in the hard kaolinitic rock from the *g* layer indicates, therefore, that the *f* layer may be considered as a B_2 horizon.

The differences in the mineralogical composition among the *a*, *b*, *c*, and *d* layers, particularly in the hornblende and biotite content, may indicate that these minerals have undergone a considerable amount of weathering, and probably they were an important source of the Fe_2O_3 that accumulated in the B horizon. The smaller amounts of biotite and hornblende in the *a* and *d* layers suggest that perhaps these layers have suffered the greatest amount of weathering. This seems also to be indicated by the presence in these layers of the largest amounts of silt and clay (table 3) and of SiO_2 (table 6).

From the preceding discussion and from the mineralogical and chemical composition of the whole soil (tables 4, 6, and 7) it may be concluded that the parent material of the profile consisted of two strata; namely, a kaolinitic shaly rock, perhaps similar to that of the *g* layer, from which the *f* layer developed; and a semiconsolidated crystal tuff from a dacitic magma (18) with, possibly, a considerable amount of free Al_2O_3 and Fe_2O_3 (a feature not unusual in such materials) which gave rise to the *a*, *b*, *c*, *d*, and *e* layers. The volcanic peaks Nevada del Tolima, Nevada del Isabel, and Nevada del Ruiz about 60 miles from Albán across the Magdalena river were most likely the source for the volcanic tuff. The relative freshness of the volcanic glass might indicate that the volcanic tuff is of a relatively recent deposit. This conclusion is not surprising in view of the fact that these volcanoes are not yet completely extinct. Whether the shaly rock is of volcanic origin is not known, but it is certain that this rock is much older than the overlying material.

Podzol nature of the profile

The most striking features of a podzol are the loss of Fe_2O_3 and Al_2O_3 from the A horizon and their accumulation in the B horizon, the accumulation of organic matter in the ortstein layer, if such is present, and the acid nature of the profile as expressed by the pH and percentage base saturation of the exchange complex (15, 16, 17). All these features are very strongly marked in the profile under discussion. The accumulation of very large amounts of Fe_2O_3 in the B horizon of this profile are indicated by the total chemical composition and by the SiO_2/Fe_2O_3 ratios (table 6). The large accumulation of Fe_2O_3, in the *e* horizon, and particularly the bleached nature of the *c* and *d* layers, are also clearly marked by the "free" iron as determined by Tamm's method (table 4). The complete absence of any iron staining on the individual mineral particles from the A_2 horizon, as observed under the microscope, is also a good indication of the bleached nature of the A_2 horizon. The accumulation of Al_2O_3 in the B horizon is clearly indicated by the SiO_2/Al_2O_3 ratios (table 6) and by the differential thermal curves (fig. 4). The differential thermal curves and the x-ray analysis indicate that a considerable amount of the Al_2O_3 has accumulated in the form of gibbsite and bauxite. The accumulation of organic matter in the ortstein layer is indicated by the total

TABLE 2

Total carbon, nitrogen, and organic matter and C/N ratios of the Sabaneta profile

LAYERS	N	C	C/N	ORGANIC MATTER			O. M.*/C	C IN ORGANIC MATTER*
				Calculated C × 1.724	Determined by H_2O_2	Determined† by ignition		
	per cent	*per cent*		*per cent*	*per cent*	*per cent*		*per cent*
a	0.88	11.45	13.1	19.94	18.02	21.8	1.91	52.5
b	0.39	6.09	15.7	10.61	8.95	13.1	2.15	46.5
c	0.23	4.33	19.1	7.54	6.33	9.7	2.24	44.7
d	0.18	2.84	15.8	4.95	4.44	6.6	2.32	43.0
e	0.12	5.02	40.5	8.74	6.94	12.4	2.47	40.5
f	0.10	1.64	16.2	2.85	2.23	4.0	2.46	41.4

* By ignition.

† A determination was made of the loss in weight of the soil when heated gradually to igniton. The loss in weight between 125 and 260°C was assumed to represent the loss of organic matter. The loss in weight below 125°C and above 260°C was assumed to represent loss in water of adsorption or crystallization.

The H_2O_2 apparently did not destroy all the organic matter. This was verified by a determination of the loss in weight of the H_2O_2-treated soil upon heating from 125 to 260°C. These losses were about equal to the differences in amount of organic matter as shown in the table.

Determination of organic matter by use of the factor 1.724 seems to be inadequate, particularly for the horizons below the surface.

carbon and organic matter content in this layer (table 2). The acid nature of the profile is also very marked particularly by the percentage base saturation (table 8). Although the pH of the surface layers of this profile may not be so low as that in some podzols (2), the percentage base saturation is certainly as low as that in the most mature podzols (17, 20, 22, 23). One other characteristic of podzols is the presence of relatively small amounts of clay in the A and B horizons (22, 23, 24). This again is true for the profile under discussion (table 3) (with the exception of the clay in the *f* layer, which merely reflects the nature of the parent material).

Although the amount of clay in the A and B_1 horizons is relatively small, its mineralogical composition is of interest. The mineralogical composition, as shown in table 5, was determined by x-ray diffraction patterns, differential thermal curves (fig. 5), and base-exchange studies (tables 5 and 9). The interest lies in the presence of a vermiculitic clay mineral as the only true clay mineral and in the presence of relatively large amounts of nonclay minerals; namely, quartz, plagioclase, and gibbsite. Perhaps the presence of a large amount of quartz and other nonclay minerals in the clay fraction (<1 μ) also may be a characteristic of colloids of other podzols. Although the proportion of vermiculite clay in the <1 μ clay fraction was large, the x-ray lines representing the vermiculite spacings—in the x-ray diffraction pattern of the <1 μ clays—were very weak no matter what pretreatment the clays received prior to x-raying. This indicated that the vermiculite clay was in a poor cyrstalline state, possibly due to its volcanic origin and the subsequent acid leaching to which it was subjected during soil formation.

TABLE 3

Mechanical analysis of the Sabaneta profile

LAYER	FRACTIONS			TOTAL
	Fine gravel and sand 2 0–0 05 mm.	Silt 0.05–0 002 mm. (50–2μ)	Clay* <0 002 mm. (<2μ)	
	per cent†	*per cent*	*per cent*	*per cent*
a	25.61	67.11	7.28	100
b	67.93	29.33	2.74	100
c	62.36	34.36	3.38	100
d	50.90	44.82	4.28	100
e	75.59	19.93	4.48	100
f	29.38	26.96	43.66	100

* Determined by the pipette method.

† Per cent based on oven-dry (110°C) and organic-matter-free soil.

As may be seen from the differential thermal curves (figs. 4, 5, 6, 7), gibbsite is present in all particle-size fractions; and from its distribution in the profile, it is clear that gibbsite is easily subject to migration. The presence of gibbsite in such an acid soil as the one under discussion is not surprising, for it was discovered that the mild acid treatment of the soils during extraction of the free

TABLE 4

Mineralogical composition[*] *of the whole Sabaneta soil*

	SOIL LAYER					
	a	*b*	*c*	*d*	*e*	*f*
Quartz[†]	38	30	19	39	11	10
Volcanic glass[‡]	34	34	40	25	10	0
Orthoclase	x	x	x	x	x	x
<2μ clay [§]	7.3	2.7	3.3	4.3	4.5	46.8
Cemented vermiculite clay	3.4	4.6	4.8	4.6	1.5	0
Biotite	1	2	4	1	2	0
Hornblende	1	2	5	2	2	0
Hypersthene	x	x	x	x	x	0
Tourmaline	x	x	x	x	x	0
Ilmenite[‖]	1	2	3	3	2	1
Gibbsite	0.3	0.7	1.0	2.0	7.0	5.5
Bauxite	0	0	0	1.0	5.0	x
Kaolinite	0	0	0	0	2	21
Leucoxene	1	1	1	2	1	1
Free R_2O_3 by Tamm's method Fe_2O_3	1.7	1.8	0.7	0.7	45.7	8.4
Al_2O_3	11.3	19.2	18.2	15.4	6.3	6.3
Total	100.0	100.0	100.0	100.0	100.0	100.0

[*] The amounts of the minerals reported were estimated as follows: gibbsite, kaolinite, and bauxite from the differential thermal curves of the whole soil; biotite, hornblende, and ilmenite by heavy liquid separation and microscopic examination; <2 μ clay by pipette analysis; cemented clay from the exchange capacity of the organic-matter–free nonclay fraction of the soil (see table 5); volcanic glass from the Na_2O content of the soil and of andesine (7.74 per cent); leucoxene from the TiO_2 and the ilmenite contents of the soil; quartz by difference.

Most of the volanic glass consisted of colorless tiny broken pieces of threads and very small irregular granules of silt size cemented together into irregular clusters. These contained the various minerals and formed the sand fractions of the soil. Other forms of volcanic glass (18, 27) were also observed. Only very little devitrification has set in. Many of the crystal forms, particularly of the hornblende, ilmenite, magnetite, and black hematite, were strikingly perfect and consisted of medium sand texture or finer. A considerable amount of secondary rust-colored hematite was also present in the *e* layer. The quartz was clear or fairly smoky in irregular fragments, rounded grains, or well-developed bipyramids with rounded edges and consisted of medium sand texture or finer. The feldspars, which were mostly andesine (as indicated by the chemical analysis of the soil and the slightly developed albite twinning), had the clear glassy appearance typical to feldspars of rhyolite, dacite, or crystal tuff (18, 27).

The cemented clay resembled the <1 μ clay in appearance and in the x-ray pattern, but seemed to contain a much larger amount of floury quartz. This material might represent volcanic mud.

X-ray analysis of the separated biotite indicated that it had an expanded lattice similar to that of vermiculite (3, 4, 5).

One of the most striking features common to all the minerals from the *a*, *b*, *c*, and *d* layers was the near absence of iron-staining.

[†] Includes amorphous SiO_2.

[‡] Includes a small amount of andesine.

[§] See table 5.

[‖] Includes magnetite and black hematite.

TABLE 5

Approximate mineralogical composition of organic-free <1 μ clay from Sabaneta soil

In percentage weight of material dried at 110°C.

LAYER	VERMICULITIC* CLAY	KAOLINITIC† CLAY	GIBBSITE†	BAUXITE†	FREE R_2O_3 BY TAMM'S METHOD		QUARTZ‡ AND AMORPHOUS SiO_2	ANDESINE‡ PLAGIOCLASE	TOTAL	H_2O (110°C.) OF THE Ca-SATURATED AIR-DRY FORM
					Fe_2O_3	Al_2O_3				
a	26	0	1	0	1.7	11.7	44.6	15.0	100.0	18.6
b	48	0	1	0	1.8	19.3	11.9	18.0	100.0	28.7
c	46	0	1	0	0.7	18.5	16.8	17.0	100.0	29.7
d	51	0	3	1	0.7	15.0	9.3	20.0	100.0	21.0
e	27	0	7	7	45.7§	6.4	3.0	3.9	100.0	15.1
f	0	68.0	2	x	7.3	5.7	17.0	0	100.0	7.6

* The identity of the vermiculitic clay was established by the 001 spacings. The spacings of the Ca-saturated clays in the air-dry, the 250°C.-heated, and the glycerol-saturated states were similar to those of vermiculite; namely, 14.5, 10.0, and 14.2 respectively. The amounts indicated in the table were calculated by assuming that the vermiculite clay was the main contributor to the base-exchange capacity of the clay and that it possessed a capacity of about 166 me. per 100 gm. dried at 110°C. (3, 4, 5). The presence of vermiculitic type clay was also indicated by the endothermic break at about 210°C. in the differential thermal curves of the soils and clays (fig. 4 and 5), by the large amount of water held at 110°C., and by the high base-exchange capacity of the <1 μ clay fraction notwithstanding the presence of large amounts of impurities with low base-exchange capacities (table 9).

† Estimated from the differential thermal curves.

‡ The sum of the quartz and andesine was determined by difference, but the amount of each was estimated from the relative intensity of the strongest x-ray lines of each mineral.

§ The Fe_2O_3 apparently was present in an amorphous form, for the x-ray diffraction diagram of the iron concretions showed only weak gibbsite lines.

TABLE 6

Chemical composition of the whole Sabaneta soil

	SOIL LAYERS											
	a		*b*		*c*		*d*		*e*		*f*	
	*	†	*	†	*	†	*	†	*	†	*	†
SiO_2(%)...	51.23	69.10	49.17	59.48	49.64	57.00	57.73	64.66	21.63	26.51	45.93	53.20
TiO_2(%)...	0.87	1.17	1.42	1.70	1.68	1.93	2.93	3.28	1.29	1.58	1.11	1.29
Fe_2O_3(%)..	2.24	3.02	2.33	2.82	3.43	3.94	3.02	3.38	40.61	49.80	7.77	9.00
Al_2O_3(%)..	13.31	18.00	23.20	28.08	24.43	28.05	20.52	23.00	15.44	18.95	29.05	33.65
MnO(%)..	0.11	0.15	0.07	0.08	0.11	0.13	0.03	0.03	trace	trace	none	none
MgO(%)...	1.72	2.32	1.69	2.04	1.54	1.77	1.33	1.49	0.71	0.87	0.80	0.93
CaO(%)...	2.29	3.09	1.97	2.38	2.86	3.27	1.67	1.87	0.85	1.04	0.62	0.72
Na_2O(%)..	1.98	2.67	2.32	2.81	2.80	3.22	1.76	1.97	0.90	1.10	0.66	0.76
K_2O(%)...	0.21	0.28	0.37	0.45	0.49	0.55	0.21	0.23	0.11	0.13	0.29	0.35
P_2O_5(%)...	0.15	0.20	0.13	0.16	0.12	0.14	0.08	0.09	0.02	0.02	0.09	0.10
Ignition (%).....	25.74		17.90		14.15		11.70		18.15		14.20	
Total(%)..	99.85	100.00	100.57	100.00	101.25	100.00	100.98	100.00	99.71	100.00	100.52	100.00
H_2O+(%).	3.9		4.8		4.5		5.1		5.8		10.2	
H_2O-(%).	17.2		22.2		20.7		17.6		19.2		12.7	
SiO_2/Fe_2O_3....	60.8		56.1		38.5		50.8		1.42		15.71	
SiO_2/Al_2O_3....	6.52		3.59		3.44		4.77		2.37		2.68	

* Per cent of whole soil oven-dried at 110°C.

TABLE 7

SiO_2, MgO, CaO, and Na_2O content of the whole Sabaneta soil

In percentage of the sum of SiO_2, MgO, CaO, and Na_2O content of the soil

LAYER	SiO_2	MgO	CaO	Na_2O	TOTAL
a	89.50	3.01	4.04	3.45	100.00
b	89.20	3.02	3.57	4.21	100.00
c	87.40	2.71	4.97	4.92	100.00
d	92.40	2.13	2.67	2.80	100.00
e	89.80	2.94	3.53	3.73	100.00
f	95.70	1.66	1.28	1.36	100.00

TABLE 8

Base-exchange properties of the whole Sabaneta soil

LAYER	NH_4-EXCHANGE CAPACITY AT pH 7.0*	TOTAL BASES	BASES, AS PER CENT OF TOTAL BASES				BASE SATURATION AT pH 7.0	pH OF SOIL
			Ca^{++}	Mg^{++}	K^+	Na^+		
	m.e.†	*me.*					*per cent*	
a	50.05	10.32	58.5	27.5	4.0	10.0	20.5	5.3
b	45.78	6.64	41.6	42.8	3.9	11.7	14.5	5.4
c	41.43	6.97	38.7	27.4	2.3	21.5	16.8	5.6
d	31.00	5.56	48.8	30.6	2.1	18.5	17.9	5.7
e	42.34	6.97	48.9	22.0	13.5	15.6	16.5	5.6
f	21.79	6.43	53.4	21.0	9.9	15.7	29.5	5.3

* The following additional determinations were made: The NH_4-exchange capacity at a pH of 8.5 and the barium-exchange capacity at a pH of 7.0. The results (in me./100 gm.) for the respective layers are as follows: 71.6, 66.5, 52.7, 38.4, 58.0, and 30.2—the NH_4-exchange capacity at pH 8.5; and 150.8, 149.4, 133.7, 112.9, 67.7, and 33.1—the Ba-exchange capacity at pH 7.0. The significance of these results will be discussed in another manuscript.

† Per 100 gm. of soil dried at 110°C.

TABLE 9

Base-exchange capacities of a few fractions of the Sabaneta soil

In milliequivalents per 100 gm. dried at 110°C.

LAYER	NH_4-EXCHANGE* CAPACITY OF <1μ CLAY†	NH_4-EXCHANGE CAPACITY OF H_2O_2-TREATED SOIL	NH_4-EXCHANGE‡ CAPACITY OF ORGANIC MATTER DESTROYED WITH H_2O_2	NH_4-EXCHANGE CAPACITY OF THE VERY FINE SAND FRACTION	NH_4-EXCHANGE‡ CAPACITY OF THE SAND + SILT
a	43.2	8.2	240.2	8.7	5.4
b	80.5	19.6	310.9	28.2	17.8
c	76.9	20.0	358.1	29.7	18.0
d	82.5	15.4	366.4	24.3	12.4
e	45.5 (80.5§)	19.8	345.0	40.9	18.6
f	25.5	13.4	390.4	21.4	4.1

* NH_4-exchange capacity with NH_4Ac at pH 7.0.

† Organic-matter-free material.

‡ Calculated values.

§ Calculated on the basis of material freed of "free Fe_2O_3."

Fe_2O_3 and Al_2O_3 did not destroy the gibbsite. On the contrary, the treated materials exhibited an enrichment of gibbsite, as was shown by the differential thermal curves of the treated materials. Whether the gibbsite is the product of podzolization associated with the weathering of plagioclase feldspars (1, 12) or was present in the parent material of the A and B_1 horizons prior to soil formation is difficult to surmise from the data at hand.

The base-exchange studies as reported in tables 8, 9, and 10, besides indicating the low base-saturation status of the soils, show:

1. The base-exchange capacity of the $<1\ \mu$ clay is very high, but its contribution to the base-exchange capacity of the whole soil is very small (except in the *f* layer).
2. The base-exchange capacity of the organic matter is very high and so is its contribution to the base-exchange capacity of the whole soil. It is interesting to note that the exchange capacity of the organic matter of the *a* layer is the smallest. Perhaps this is due to the presence in this layer of a considerable amount of coarse and only partly decomposed organic matter.
3. The sand and silts have a considerable base-exchange capacity, and their contribution to the base-exchange capacity of the soil is substantial. The base-exchange capacity of the sands and silts may be due to the cemented clay.

TABLE 10

Percentage contribution of organic matter, $<2\ \mu$ clay, and sand + silt fraction to the NH_4-exchange capacity (at pH 7.0) of the whole Sabaneta soil

LAYERS	CONTRIBUTION OF ORGANIC MATTER	CONTRIBUBUTION OF $<2\mu$ CLAY	CONTRIBUTION OF SAND + SILT	TOTAL
a	87.0	4.8	8.2	100.0
b	60.8	4.4	34.8	100.0
c	54.2	6.7	39.1	100.0
d	52.3	11.0	36.7	100.0
e	56.3	4.7	39.0	100.0
f	40.0	49.3	10.7	100.0

GENERAL DISCUSSION

Although the parent material of the Albán profile proved to be stratified, the results presented herein, particularly the nature of the distribution of gibbsite, free Fe_2O_3, and organic matter, indicate that the profile itself is of a truly genetic origin.

The results also show that the profile possesses all the properties of true podzols, as they are known in the Northern Hemisphere, but with unusually thick A_1 and A_2 horizons and with an extremely large accumulation of Fe_2O_3 in the B_1 horizon. The presence of an extensive A_1 horizon might suggest that the profile should be classified as a gray-brown podzolic soil as described by Marbut (24). The presence, however, of a very strongly bleached horizon and a distinct ortstein horizon definitely excludes the profile from the gray-brown podzolic group of soils. An explanation for the formation of an extensive A_1 horizon perhaps may be found in the presence of a very abundant ground vegetation with a relatively shallow root system, as may be seen in figure 2. Such an abundant ground vegetation would undoubtedly enrich the surface layer of the mineral soil with a great amount of organic matter by root growth. A similar condition of podzol development was encountered recently in the high Sierra-Nevada Mountains of California under grass vegetation (fig. 3). In this profile too, a distinct A_1 horizon has developed above the strongly bleached A_2 horizon. The cause was clearly observed to be the abundant shallow root system of the grasses.

TABLE 11

Base-exchange properties of a few acid soils from Colombia

SOIL	DEPTH	NH_4-EXCHANGE CAPACITY AT pH 7	TOTAL BASES	PER CENT BASE SATURATION	BASES, AS PER CENT OF TOTAL BASES				Ba^{++} EXCHANGE CAPACITY AT pH 7.0	pH	N	C
					Ca^{++}	Mg^{++}	K^+	Na^+				
	inches	*me.**	*me.*						*me.*		*per cent*	*per cent*
Calima profile No. 76 (13)	0–2	35.51	3.67	10.4	32.4	33.3	15.5	18.8	—	4.6	1.03	20.75
	2–8	25.59	2.35	9.2	36.6	32.8	5.5	25.1	—	5.2	0.49	7.20
	8–18	24.04	1.70	7.1	24.1	30.0	8.8	37.1	—	5.4	0.39	5.23
	18–25	9.34	1.79	19.2	32.4	27.9	7.8	31.9	—	5.2	0.08	0.87
Agricultural Forest Experiment Station, of Calima	surface†	29.30	1.78	6.1	39.9	30.3	19.1	10.7	58.8	4.7	—	—
	subsoil†	18.35	2.80	15.3	66.8	20.4	6.4	6.4	38.8	5.3	—	—
Sample no.:												
17.750‡	—	73.96	6.74	9.1	60.2	22.7	1.7	15.4	139.8	4.4	1.21	17.69
17.791	—	63.58	6.60	10.4	39.1	45.7	4.3	10.9	82.9	5.2	0.27	7.23
17.713	—	64.45	12.12	19.2	61.1	20.5	11.5	6.9	121.8	5.2	0.71	17.55
17.593	—	63.00	2.88	4.6	18.1	35.4	26.7	19.8	112.7	4.3	0.73	14.58
17.594	—	61.26	2.81	4.6	21.4	16.0	27.4	35.2	87.1	4.1	0.72	12.70
17.595	—	12.29	2.15	17.5	26.5	15.7	18.4	39.4	23.5	4.7	0.08	3.79

* Per 100 gm. of soil dried at 110°C.

† Depths not indicated by collector.

‡ Location and depth not indicated by collector of these samples.

The chemical and mineralogical analyses of the Albán profile indicate that, as in other podzols (6, 7, 24, 29), formation of the bleached A_2 horizon does not necessarily involve the entire disappearance in the horizon of all of the primary minerals such as hornblende, biotite, hypersthene, and feldspars. They also illustrate that the essential process in the formation of the bleached horizon is a removal of the free Fe_2O_3 and at least some of the free Al_2O_3 which either were originally present or were formed during the weathering of minerals containing these oxides.

The dimensions of the various horizons of podzol profiles would be expected to vary and to depend upon the soil-forming factors. Thus the giant dimensions of the A_1 and A_2 horizons of the Albán profile might be explained possibly by the following soil-forming factors conducive to intense leaching and bleaching:

1. A parent material consisting of a very permeable tuff high in free Al_2O_3 and Fe_2O_3, high in both total and exchangeable bases, and underlain by a kaolinitic shaly rock of a much lower permeability.
2. A gently sloping topography.
3. An annual rainfall of about 80 inches coupled with a uniform annual temperature of about 63°F.[2]
4. A luxuriant plant growth throughout the year yielding large amounts of organic matter for decomposition.

The presence of a kaolinitic layer with a relatively low permeability at some distance below the surface might have helped to trap the percolating solutions at the boundary line between the two kinds of parent material and to have confined most of the deposition of the Fe_2O_3 to the relatively thin B_1 horizon. On steeper slopes, and where the kaolinitic layer was closer to the surface, shallower podzol profiles were observed and mapped (28), as shown in figure 2.

One of the most interesting findings revealed by the base-exchange studies of the Albán profile, and of other very acid soils from Colombia (table 11), is that notwithstanding the very low state of base saturation, these soils support luxuriant plant growth [as indicated by the high N and C content of these soils and by actual measurements of organic matter production (14)]. An explanation for this condition possibly may be found in Graham's work (8, 9, 10, 11) in which the showed that in presence of large amounts of exchangeable H^+ (whether on organic or inorganic exchange materials) nonexchangeable bases of primary minerals become available for plant uptake.

SUMMARY

Chemical, mineralogical, and base-exchange studies have confirmed the presence of a podzol of giant dimensions in the cool climate of the high mountains of the equatorial region of Colombia, South America.

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[2] It is interesting to note that the mean temperature for the frost-free period (May to September) in the southern part of the podzol region of North America (Minnesota, Wisconsin, Michigan, and New Hampshire) is also about 63 to 64°F. (25). This suggests, perhaps, that the processes involved in podzol formation are active mainly during the frost-free period of the year. This suggestion may have some merit, since two of the factors important in soil-forming processes—leaching, which involves water, and the supply of organic substances, which combine with free Fe_2O_3 for removal from the A_2 horizon—depend upon temperatures above freezing.

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POTASSIUM-SUPPLYING POWER OF SEVERAL INDIANA SOILS[1]

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Received for publication January 24, 1950

It is a common observation that soil types vary in their ability to supply potassium to plants. The readiness with which a soil releases nonexchangeable potassium to the exchangeable form is a characteristic often referred to as the potassium-supplying power.

A study was undertaken to determine the potassium-supplying power of 23 Indiana soil types as determined by continuous cropping with ladino clover in the greenhouse. In addition, the effect of added potassium on the potassium-supplying power of 10 of the more important soils, as measured by plant uptake, was studied.

LITERATURE REVIEW

A number of explanations have been suggested for the processes involved in the reciprocal transformations of exchangeable and nonexchangeable potassium (2, 3, 4, 6, 7, 8, 9, 10, 11). The exact nature of these processes is not known. It is now generzlly accepted, however, that an equilibrium exists among water-soluble, exchangeable, fixed or nonexchangeable, and primary mineral forms of potassium. The evidence indicates that the nature of this equilibrium is variable and depends upon the soil type or nature of clay minerals present.

DeTurk, Wood, and Bray (5) proposed a two-phase equilibrium between the soil solution and exchangeable potassium and between exchangeable and nonexchangeable potassium. They reported that these equilibria can be forced in either direction by altering the concentration relations, but in each the soil tends to attain its inherent "equilibrium level" of exchangeable potassium. They recognized two forms of fixed potassium: one was dissolved by boiling for 10 minutes in N HNO_3, and the other was in the insoluble residue. They also found that the content of the soluble form was directly related to the potassium-supplying power of the soil. Potassium fixation was thought to be a beneficial process, since fixed potassium is held against leaching but becomes available to crops under suitable conditions.

When potassium is applied to the soil, it changes from the water-soluble to the exchangeable form, and, if not utilized by plants, it may become fixed by the soil colloids in a nonexchangeable form. For any given soil type, the extent to which fixation occurs depends upon the potassium level of the exchange complex; the higher this level, the greater is the fixation (5). "Potassium fixation" has generally been considered to mean conversion from exchangeable to nonexchangeable forms. The amount fixed, as well as the addition required to bring about fixation, varies with different soils, depending on the amount of colloid in the different soils, particle size distribution, potassium content, mineralogical constitution of the colloid, and perhaps other factors (5).

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[1] Journal Paper No. 441 Purdue University, Agricultural Experiment Station, Lafayette, Indiana. Contribution from the department of agronomy. Part of a thesis presented by the senior author in partial fulfillment of the requirements for master of science degree. The authors are indebted to M. L. Jackson, formerly of this department, for supervision of the initial phases of this research. Acknowledgment is made to the American Potash Institute for fellowship funds that made this study possible.

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Attoe and Truog (1) divided the potassium of the soils into three categories based upon its availability to plants. These included the readily available, water-soluble, and exchangeable forms of potassium; the moderately available or fixed and biotite forms; and the difficultly available or feldspar and muscovite forms. The moderately available forms of potassium were those which were nonexchangeable but soluble when extracted for one hour with 0.5 *N* HCl.

Stewart and Volk (14) found that an average of two thirds of the potassium used by the plants came from forms that were nonexchangeable at the beginning of the experiment, and the amount of nonexchangeable potassium removed from the different soils varied between 39 and 87 per cent of the total amount of potassium consumed by the plants. No close relationship was found between the potassium removed by the crops and the exchangeable potassium in the soil, removed from the soil, or remaining in the soil after cropping.

PROCEDURE

The soils for this investigation comprise 23 of the major soil types of Indiana[3], representing about 13 million acres, or approximately 54 per cent of the agricultural land of the state. They are typical of a wide range of soil conditions such as are found in many parts of the corn belt.

The samples were procured by using a random sampling technique. Several 1-inch cores of soil were taken over an area of about 1 acre. For each soil type, three composite samples from fields in cultivation spaced at least a mile apart were taken at each of three depths, 0–6, 6–12, and 12–18 inches, for laboratory analysis. The sites selected were in areas where the particular soil type was extensive. The fertilizer treatment history of the soils was not known but was assumed to be average for the soil type. The exchangeable potassium was determined on all three soil samples from each depth. At each selected site, bulk samples were taken from the 0–6-inch layer of soil for the greenhouse experiment. All soil samples were crushed to pass a quarter-inch sieve and were thoroughly mixed.

The soil samples used for laboratory analysis were stored field-moist at room temperature. The bulk samples of soil were used for greenhouse work after lime and fertilizer had been added.

The exchangeable potassium in the soil was determined by leaching with neutral normal ammonium acetate solution and precipitated by the sodium cobaltinitrite colorimetric method.[4] The plant material was dry-ashed (12), and total potassium content was determined on a Perkin-Elmer flame photometer (model 52A) using 100 ppm. of lithium nitrate as the internal standard. All analyses were calculated on an oven-dry basis.

The lime requirement to pH 6.5 was determined for each soil, and 100-mesh dolomitic limestone was added as needed to adjust the soils to that value. Supplemental fertilizer was added, on a per-acre basis, in the following amounts: 300 pounds P_2O_5, and 20 pounds N as starter for ladino clover. No potassium was applied except in the special experiment to study the effect of added potassium upon the potassium-supplying power of the soil. Minor element needs were taken care of by the following application, on a per-acre basis: 10 pounds $ZnSO_4$, 5 pounds $Na_2B_4O_7$, 25 pounds $MnSO_4$, 50 pounds $CuSO_4$, 1 pound $(NH_4)_6Mo_6O_{24} \cdot 4H_2O$, and 2 pounds $CoCl_2$. The limestone and supplemental fertilizer were thoroughly mixed with each lot of soil before it was placed in the cans used for greenhouse tests. In addition to the experiment on the original soils as sampled, the effect of potassium fertilization (75 and 200 pounds K_2O per acre) upon the supplying power was studied on 10 of the more important soil types. At least three replications were made in all cases. Sufficient additional replications were made on 10 of the soil types so that pots could be sacrificed to analyze for exchangeable potassium on the soils after the third, fourth, and sixth cuttings as well as after the eighth. The clover was cut as soon as the plants on any one treatment appeared to be ready to set seed. This was used as the guide to keep the plants in the vegetative stage.

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[3] For description of these soils see Bushnell, T. M. The story of Indiana soils. Purdue Agr. Exp. Sta. Spec. Cir. 1. 1944.

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The experiment was set up and the ladino clover planted on July 23, 1946. The crops grew continuously for 493 days, and produced eight cuttings. The experiment was discontinued November 27, 1947. For analysis, the plant material was composited into two large samples: the first four cuttings and the last four.

Tin cans, with varnished interiors, commonly sold as size No. 1 with a capacity of 12 fluid ounces, were used instead of pots in the greenhouse studies. Preliminary investigations indicated that there was no particular advantage in using larger containers for this experiment. Glass tubes were placed in the containers for aeration and to facilitate watering. A layer of quartz sand was placed at the bottom of the can and the glass tube placed upright in the sand, so the water was evenly distributed on the bottom of the soil. The container plus the glass tube was brought up to a tare weight of 100 gm. by addition of quartz sand. The soil was then added, and enough quartz sand placed on top of the soil to counterpoise each can to a uniform weight. The soils were watered at least once a day and brought up to the optimum water content.

RESULTS AND DISCUSSION

The exchangeable potassium content of the surface 6 inches of these soils varied from 89 to 253 pounds K_2O (table 1). In 6–12 inch layer, the range was 28 to 240 pounds, and for the 12–18-inch layer it was 25 to 161 pounds. The exchangeable potassium content was highest in the surface 6 inches in all but three soils—the Frederick, the Fairmount, and the Genesee.

The soils producing the highest yields of clover with no added potassium were: Fairmount, Genesee, Fox silt loam, Nappanee, Russell, Crosby, and Chalmers. All of these yielded more than 8 gm. of oven-dry material from the eight harvests. Though the largest yields of clover also removed the greatest amount of nonexchangeable potassium from the soil, this relationship was not consistent. For example, although Fox and Crosby silt loams removed 531 pounds of nonexchangeable K_2O per acre, as compared to 1023 for Fairmount, their yields were not so strikingly different from Fairmount. This suggested that some other factor than potassium may also have limited growth in some instances. Larger quantities of plant material were removed from all soils in the first cutting than from any subsequent cutting. By the seventh cutting, the weight of plant material produced from all soils had reached a low but fairly constant level.

TABLE 1

Exchangeable potassium of the original soil samples

SOIL NO.	SOIL TYPE	K_2O PER ACRE 0–6 in.	6–12 in.	12–18 in.
		lb.	*lb.*	*lb.*
1	Miami silt loam	153	87	72
2	Nappanee silt loam	232	99	81
3	Newton loamy fine sand	145†	108	51
4	Houghton muck*	141	36	70
5	Fincastle silt loam	197	90	50
6	Crosby silt loam	143	92	77
7	Cincinnati silt loam	160†	67	63
8	Chalmers silty clay loam	149	60	45
9	Clermont silt loam	89	28	35
10	Frederick silt loam	117	205	161
11	Philo silt loam	149	63	55
12	Zanesville silty clay loam	145	118	95
13	Fox silt loam	253	140	100
14	Bedford silt loam	155†	98	67
15	Alford silt loam	153	55	52
16	Brookston silty clay loam	100†	37	31
17	Fairmount silty clay loam	143	240	91
18	Parr silt loam	150	85	79
19	Fox sandy loam	154	102	47
20	Genesee silt loam	131	149	114
21	Vigo silt loam	107†	42	71
22	Russell silt loam	166	85	93
23	Maumee fine sandy loam	100†	51	25

* Weight of Houghton calculated at 760,000 pounds per acre 6 inches of surface soil, all others at 2,000,000 pounds.

† Analysis made by R. D. Rouse on bulk composite samples stored in field-moist condition.

The potassium removed by cropping with ladino clover, the exchangeable potassium remaining in the soil after eight crops, and the potassium released from the nonexchangeable to the exchangeable form during the cropping period are shown in table 2. The total potassium in each soil is also presented for comparison. The Maumee was the only soil that apparently fixed part of the potassium which was exchangeable at the beginning of the experiment. The amount seemingly fixed was only 18 pounds, which might be due to experimental error. Nevertheless, this soil obviously has a very weak potassium-supplying power.

TABLE 2

Summary of the potassium-supplying power of the soils with no potassium added, as indicated by extraction by ladino clover, eight cuttings in 493 days

SOIL NO.	SOIL	EXCHANGEABLE K_2O			NONEXCHANGEABLE K_2O* Released by soil	TOTAL K_2O
		Original in soil	Removed by crops†	Final in soil		
		lb./A.	*lb /A.*	*lb./A.*	*lb./A.*	*lb./A.*‡
1	Miami	153	415	42	304	43,500
2	Nappanee	232	815	60	643	44,500
3	Newton	145	210	35	100	22,000
4	Houghton§	141	273	35	168	6,500
5	Fincastle	197	439	44	286	33,000
6	Crosby	143	633	41	531	40,000
7	Cincinnati	160	490	37	367	42,500
8	Chalmers	149	854	88	793	34,000
9	Clermont	89	182	29	121	24,500
10	Frederick	117	734	53	670	50,500
11	Philo	149	640	51	542	38,000
12	Zanesville	145	445	49	349	37,500
13	Fox silt loam	253	703	82	532	42,500
14	Bedford	155	416	42	303	34,000
15	Alford	153	354	49	250	38,000
16	Brookston	100	674	57	631	38,500
17	Fairmount	143	1043	123	1023	62,500
18	Parr	150	439	85	374	39,000
19	Fox sandy loam	154	223	23	92	45,500
20	Genesee	131	923	135	927	40,000
21	Vigo	107	270	42	215	37,500
22	Russell	166	783	66	683	45,000
23	Maumee	100	34	48	−18‖	23,500

* Nonexchangeable K_2O represents the potassium-supplying power.

† It is assumed in this table that the potassium used by the crop was the exchangeable.

‡ Analyses made by the agronomy department analytical laboratory.

§ Calculated on basis of 760,000 pounds per acre 6 inches of surface soil; all others calculated on basis of 2,000,000 pounds.

‖ Fixation, or perhaps experimental error.

The amounts of potassium that were released from the nonexchangeable to the exchangeable form, or were made available to the plants during the cropping period, varied from 92 pounds for Fox sandy loam to 1023 pounds for Fairmount silty clay loam. There was no correlation at the 0.05 (*P*) level between the amount of potassium originally in the soil and the amount released from the nonexchangeable to the exchangeable form.

To study the changes in exchangeable potassium that occurred as the cropping progressed, analyses were made after three, four, six, and eight harvests on 10 of these soils (table 3). Obviously, cropping reduced the exchangeable potassium to a rather constant level early in the cropping sequence, and thereafter the plants were dependent upon the rate at which potassium was converted from the nonexchangeable to the exchangeable form. This rate is the potassium-supplying power of the soil and is peculiar to each soil type. It is noteworthy that the Chalmers, Frederick, and Brookston soils were able to maintain their supply of exchangeable potassium considerably better than the others. After the heavy cropping, the exchangeable potassium remaining in these soils ranged from approximately 20 to 60 per cent of the original values.

TABLE 3

Exchangeable potassium content of 10 soils before and after cropping for 493 days

SOIL NO.	SOIL	EXCHANGEABLE POTASSIUM (K_2O)*					
		Original in soil	After crop 3	After crop 4	After crop 6	Final after crop 8	Percentage of original removed
		lb./A.	*lb./A.*	*lb./A.*	*lb./A.*	*lb./A.*	*per cent*
1	Miami	153	47	56	46	42	73
4	Houghton	141	35	37	41	35	75
5	Fincastle	197	43	52	48	44	78
6	Crosby	143	50	93	61	41	71
7	Cincinnati	160	79	76	44	37	77
8	Chalmers	149	84	89	91	88	41
10	Frederick	117	74	51	60	53	55
16	Brookston	100	50	87	76	57	43
21	Vigo	107	54	39	61	42	61
22	Russell	166	110	94	48	66	60

* Based on 2,000,000 pounds of soil per acre 6 inches of surface soil, except Houghton, at 760,000 pounds.

Rouse and Bertramson (13) showed that the correlation between exchangeable potassium originally in the soil and the potassium-supplying power was very low. The correlation coefficient was 0.18 for all 23 soils. The data presented here show, however, that after 10 of these soils were intensively cropped until three cuttings were removed there was a rather close relationship between the exchangeable potassium level (table 3) and the potassium-supplying power or nonexchangeable potassium released (table 2). The correlation coefficient[5] was 0.67. The correlation coefficients between exchangeable potassium after four, six, and eight cuttings and the potassium-supplying power are 0.75, 0.68, and 0.83, respectively. These close correlations indicate that under such intensive cropping conditions, the level of exchangeable potassium in the soil is a good indicator of the potassium-supplying power. The chief weakness of this indicator is that intensity of cropping is a variable factor which is difficult, or impossible, to control or to evaluate accurately under field conditions.

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[5] Acknowledgment is made to S. R. Miles, Purdue statistician, and his staff for these tatistical analyses.

The amount of potassium released from the nonexchangeable to the exchange-above form seems very large for some of the soils studied. The crop in these experiments was grown through eight successive harvests under greenhouse conditions in which the experimentally designed limiting factor in the first series of pots was a lack of potassium. This deficiency was partly alleviated in the second and third experiments by applications of KCl equivalent to 75 and 200 pounds of K_2O per acre respectively.

When KCl was added at the rate of 75 pounds of K_2O per acre on 10 of the soils, yields increased on six of them. The addition of K_2O gave an increased yield of plant material for the first crop on the Miami, Fincastle, Crosby, Chalmers, Frederick, Brookston, and Vigo soils. Potassium-deficiency symptoms began to appear after the second crop; and after the third crop virtually all plants were showing deficiency symptoms. The additional potassium increased the yields of plant material only temporarily, and then the yields on soils having a low potassium-supplying power began to decrease because of the inability of the soil to release the potassium from the nonexchangeable to the exchangeable form fast enough to supply the plant needs.

The percentage increase in yield of plant material following addition of the 75 pounds of K_2O was greatest for Brookston, 17 per cent. A 7 per cent yield increase was obtained on Fincastle. The total yield of plant material changed very little on the other soils, with the exception of that on Russell, which decreased 12 per cent. Apparently some other factor than potassium availability was involved in this case, because with the 200-pound application of K_2O this soil gave an increased yield over the original untreated soil.

In this study, the data were interpreted as though the added K_2O lost its identity entirely and merely became a part of the potassium-supplying power system of the soil. The increase in potassium removal was interpreted, therefore as a momentarily greater supplying power of the soil. One might consider that the large amount of available K_2O resulting from these additions of K_2O shifted the equilibrium toward less supplying power while the plants fed on the added K_2O as the exchangeable form. Though neighter consideration is entirely correct, it was believed the former is more nearly so.

The potassium-supplying power of these soils, enhanced initially with a 75-pound application of K_2O is summarized in table 4. The smallest amount, 209 pounds K_2O per acre, was released by Houghton; the largest amount, 677 pounds, was released by the Frederick soil. Only three of the 10 soils failed to increase their potassium-supplying power as a result of the application. Of the seven soils showing an increase, only two, Crosby and Cincinnati, showed an increase greater than the 75 pounds of K_2O added.

Addition of KCl at the rate of 200 pounds K_2O per acre increased the total yield of ladino clover on all soils except the Chalmers. Many of these increases were small and obviously nonsignificant. The amount of plant material produced from the first crop increased, but by the seventh crop the amount had reached a fairly constant level on all soils. The Miami, Crosby, Chalmers, Brookston, and Russell soils were the highest producers of plant material. Potassium-deficiency symptoms began to appear after the fourth crop and were very common after the fifth.

TABLE 4

Summary of potassium-supplying power of the soils with addition of 75 pounds K_2O per acre

SOIL NO.	SOIL	EXCHANGEABLE K_2O			NONEXCHANGEABLE K_2O	
		Original in soil	Removed by crops*	Final in soil	Released by soil†	Increase in amount released over no K_2O
		lb./A.	*lb./A.*	*lb./A.*	*lb./A.*	*per cent*
1	Miami	153	424	38	309	2
4	Houghton‡	141	326	24	209	24
5	Fincastle	197	448	28	279	−2
6	Crosby	143	737	34	628	18
7	Cincinnati	160	600	52	492	34
8	Chalmers	149	730	63	644	−19
10	Frederick	117	740	54	677	1
16	Brookston	100	714	48	662	5
21	Vigo	107	284	67	244	14
22	Russell	166	690	52	576	−16

* It is assumed in this table that the potassium used by the crop was the exchangeable.

† In these figures, no deduction has been made for the 75 pounds of K_2O added per acre.

‡ Calculated on basis of 760,000 pounds per acre 6 inches of surface soil; all others calculated on basis of 2,000,000 pounds.

Application of potassium at the higher rate greatly increased the apparent potassium-supplying power of the soils (table 5). The greatest increases in plant material produced were from Fincastle, 27 per cent, and from Vigo, 23 per cent. During the 493-day cropping period, Crosby released the most potassium, 822 pounds, and Houghton, the least, only 295 pounds. If the 200 pounds of K_2O added in the exchangeable form were subtracted from the amount considered to be released by the soil originally, only one soil, the Crosby, indicated a release of more potassium from the nonexchangeable to the exchangeable form than where no potassium was added. On all other soils, either part of the added potassium was fixed, or the equilibrium shifted in the other direction and the soils did not release as much potassium as when none was added. Since the added potassium enters into equilibrium with the various forms in the soil, it was considered not as remaining in the available form to be deducted from the potassium-supplying power, but rather, as entering into the capital stock of the soil reserves and becoming an integral part of the potassium-supplying power.

In all cases the plants removed more potassium than can be accounted for by the decrease in exchangeable potassium. The fact that such a large and variable amount of nonexchangeable potassium becomes exchangeable and is utilized by the plants likely accounts for the poor relationship between the exchangeable potassium in the soils and the response of plants to applications of potash.

The apparent amount of potassium released from the nonexchangeable to the exchangeable form was greatest for Houghton, with an increase of 75 per cent, followed by Crosby, with an increase of 55 per cent. The only decrease, or fixation, was in the Chalmers soil, 10 per cent. As the increase in exchangeable potassium does not account for all the K_2O added, a portion was apparently fixed.

TABLE 5

Summary of potassium-supplying power of the soils with addition of 200 pounds K_2O per acre

SOIL NO.	SOIL	EXCHANGEABLE K_2O			NONEXCHANGEABLE K_2O	
		Original in soil	Removed by crops*	Final in soil	Released by soil†	Increase in amount released over no K_2O
		lb./A.	*lb./A.*	*lb./A.*	*lb./A.*	*per cent*
1	Miami	153	528	37	412	35
4	Houghton‡	141	400	36	295	75
5	Fincastle	197	585	48	436	53
6	Crosby	143	924	41	822	55
7	Cincinnati	160	660	31	531	45
8	Chalmers	149	778	88	717	−10
10	Frederick	117	796	59	738	10
16	Brookston	100	682	56	638	1
21	Vigo	107	368	48	309	44
22	Russell	166	878	45	757	10

* It is assumed in this table that the potassium used by the crop was the exchangeable.

† In these figures, no deduction has been made for the 200 pounds of K_2O added per acre.

‡ Calculated on the basis of 760,000 pounds per acre 6 inches; all others calculated on basis of 2,000,000 pounds.

SUMMARY

The potassium-supplying power of 23 Indiana soils was determined by intensive cropping (eight cuttings of ladino clover) in the greenhouse. The removal of potassium by the plants beyond that accounted for by a decrease in exchangeable potassium was called the "potassium-supplying power."

Upon continuous cropping with ladino clover, the exchangeable potassium content of the different soils decreased very rapidly at first, then more gradually until a certain level was reached when the potassium-supplying power of the soils was determined largely by the rate at which the nonexchangeable potassium was converted into the exchangeable, which was considered the form available to the plants. After three cuttings of ladino clover, the soils had reached a fairly low level of exchangeable potassium, which remained rather constant through the remainder of the experiment. The amount of exchangeable potassium in the soil at this level under intensive cropping gave a close correlation with the potassium-supplying power. The correlation coefficient for the average exchangeable potassium after the three, four, six, and eight cuttings and the potassium supplying power is 0.92.

The plants caused a large quantity of nonexchangeable potassium to be extracted from the soils, yet no relationship was found between the potassium removed by the crops and the exchangeable potassium in the soil initially, removed from the soil, or remaining in the soil after cropping. No relationship was found between the total potassium content of the soils and their potassium-supplying power.

The ability of different soils to release potassium from the nonexchangeable to the exchangeable forms for plant consumptoin appears to be a dominant factor in the nutrition of plants and is a characteristic of each soil type.

The effect of an addition of 75 pounds of K_2O per acre upon the potassium-supplying power of 10 soils was studied. Although increases in yield of ladino clover on six of the soils were obtained, seven showed an increase in the amount of potassium released from the nonexchangeable to the exchangeable form.

When potassium was added at the rate of 200 pounds of K_2O per acre, the yield of ladino clover increased on nine of the 10 soils used. Nine of the 10 soils showed an increase in the amount of potassium released from the nonexchangeable to the exchangeable form.

The Chalmers soil differed markedly from the others, apparently having a capacity for very rapid adjustment in equilibrium, which makes it quite independent of potassium fertilization at its present state of fertility.

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SOIL SCIENCE

VOLUME 70 October 1950 NUMBER 4

RELEASE OF SODIUM FROM NONREPLACEABLE TO REPLACEABLE FORMS IN SOME IOWA SOILS[1]

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Received for publication March 2, 1950

The chemistry of Na in soils has received little attention other than from investigators concerned with effects of excess of the element in alkali soils. The forms in which Na is found in soils of humid regions and the conversions from one form to another in such soils are not well understood. Recent interest in the value of this element in plant nutrition has indicated a need for information on the factors affecting the Na-supplying power of soils.

It has been established that certain crops absorb fairly large quantities of Na from soils which contain relatively small quantities of the replaceable and water-soluble forms (3). For example, in greenhouse experiments, a Webster soil from Iowa that contained 16 ppm. of replaceable Na produced beets containing 0.68 per cent Na, and the total uptake by the crop was equivalent to 60 per cent of the original replaceable Na in the soil.[2] Such data indicate that the replaceable Na is replenished at a significant rate in such soils. The investigation reported here was conducted to determine how much replaceable Na is contained in Iowa soils and how rapidly sodium from nonreplaceable forms is released to replaceable and water-soluble forms.

The soils used in this investigation were selected to present a range in degree of horizon development. They were formed from somewhat different parent materials and included both grassland and timbered soils. It was hoped that results from this range of soil types might provide some information on the effect of various soil-forming factors upon Na release.

The release of K from nonreplaceable forms was also measured in these same soils. Since the release of nonreplaceable K has been studied in some detail, it seemed possible that comparisons of the rate of release of K and Na might aid in interpretation of the results.

MATERIALS AND METHODS

Soils studied

Thirteen soil profiles in widely different parts of Iowa were selected for Na-release studies. Three horizons from each profile were chosen and usually represented the A, the A_2 or A-B transition, and the B horizon.

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[1] Journal Paper J-1759 of the Iowa Agricultural Experiment Station, Ames, Project 624.

[2] Larson, W. E. Release of sodium from nonreplaceable to replaceable forms in Iowa soils and the response of various crops to sodium fertilization. 1949. [Unpublished Ph.D. thesis. Copy on file Iowa State College, Ames]

A group of soils from a "loess traverse" in southern and western Iowa were among those chosen. The genesis of these soils has been studied by Hutton (6) and Ulrich (13). Arranged in order of increasing horizon development, they are the Marshall, Sharpsburg, Haig, Seymour, and Edina series. These soils were all formed from loess, the source of which is believed to have been the Missouri River bottoms. Similar groups of loess-derived soils from Illinois have been described by Smith (11). Taintor soils were developed from a loess which apparently originated from a central Iowa source. They resemble the Sharpsburg soils in that they show only moderate development of a textural B horizon but differ in that they have darker colored surface horizons and are found on more nearly level sites.

The Fayette, Weller, and Marion soils were formed under forest vegetation. Fayette soils occur on moderate slopes from loess originating in connection with the Iowan till plain and show little horizon differentiation. Weller soils are found on gently rolling slopes and are formed from loess which is thinner and from a different source from that from which the Fayette soils are formed. Weller soils have definite A_2 horizons with very fine textured B horizons. Marion soils are the most highly developed of the forested soils used here. They are found on flat areas in association with the Weller soils, and have thick, ashy A_2 horizons and extremely dense B horizons.

The Webster, Carrington, and Floyd series were formed under grass vegetation. Webster soils are developed on glacial till of the Mankato substage of the Wisconsin glaciation. They have very dark colored surface horizons with a moderately fine textured, poorly oxidized B horizon. They occur on nearly level sites in north central Iowa. Carrington and Floyd soils were developed from a mixed thin covering of loess and till overlying very slowly permeable Iowan till. Floyd soils are found on lower, more nearly level sites and have slightly finer textured B horizons than Carrington soils.

Laboratory methods

The Na and the K released from nonreplaceable forms were measured by determining the amounts of these ions in replaceable forms at various periods following removal of all replaceable bases. The replaceable bases were removed by leaching 100-gm. samples of the soils with normal NH_4OAc until the leachate was free of Ca. This was followed by a leaching with H_2O, then one with 0.1 *N* acetic acid, and finally by another leaching with H_2O. The H-saturated soils were then dried at room temperature, crushed, and mixed. One aliquot of soil was removed for analysis to determine the amounts of replaceable cation remaining in the leached soil. The remainder of the sample was moistened to field capacity and placed in waxed cartons, where it was allowed to incubate at room termperature. The moisture content was maintained at field capacity. Samples for analysis were removed at the end of 60, 180, and 360 days. Replaceable Na and K were extracted by leaching 25-gm. samples of soil with 400 ml. of neutral normal ammonium acetate on a Büchner funnel. The samples removed for analsis during the incubation period were not dried prior to extraction for replaceable Na and K.

Na was precipitated with magnesium uranyl acetate according to Peech (9), centrifuged, washed, and weighed in the centrifuge tubes. K was determined by the method of Brown *et al.* (4). A glass electrode was used for pH measurements. All determinations were made in duplicate.

RESULTS

The amounts of Na and K present in replaceable forms in the untreated soils and at various periods during the incubation are shown in table 1. Under the conditions of this experiment, more Na than K was generally released in 360 days even though less Na than K was originally present in the replaceable form in the untreated soils. Most of the surface soils released more Na in 360 days than was originally present in replaceable form in the untreated soils. This was also generally true of the B horizons of most of the soils that do not have highly developed fine textured B horizons (Fayette, Sharpsburg, Taintor, Carrington, and Webster). On the other hand, the soils that have claypans or show a tendency toward claypan development, such as the Haig, Seymour, Edina, Weller, and Marion soils, originally contained much more replaceable Na in the B horizon than was released in this same horizon in 360 days.

The magnitude of Na release with depth in the profile showed no pronounced trend for all soils. Of the 13 profiles, eight showed a higher release of Na from the A horizon than from the B horizon, but the averages for all soils of Na release from the A and B horizons in 360 days were almost the same. In contrast to this, the release of K from the same soils showed a distinct trend with depth in the profile. In 11 of the 13 soils the release of K was greater from the A horizon than from the B horizon in 360 days. The A horizons released an average of 0.16 me. K per 100 gm. in 360 days, while the B horizons released only 0.11 me.

Figure 1 shows the average rates of release of Na and K with time for the A and B horizons of all soils. Generally, Na release was most rapid during the first 60 days of incubation, followed by a slightly slower rate during the next 120 days. In some cases the release continued at a nearly linear rate throughout the incubation period, while in others the rate of release was very slow after the first 180 days. The rate of K release with time was quite different from that of Na. An appreciable amount of K was rendered replaceable during approximately the 1-day drying period following removal of all replaceable bases. Evidence that this was real and not the result of an incomplete extraction of the original replaceable K lies in the fact that other cations were found, on analysis, to be rather completely removed. Another considerable amount of K was released during the first 60 days of incubation, and smaller amounts were released after that time. An average of 48 per cent of the total potassium released was released during the drying period. In all but three cases, more K than Na was released during the first 60 days of incubation, whereas more Na than K was released in all except one case during the last 300 days of incubation.

TABLE 1

Release of sodium and potassium from nonreplaceable to replaceable forms during 360 days' moist incubation

FILE NO.	SOIL	HORIZON	DEPTH	pH OF INCUBATED SAMPLE		ORIGINAL REPLACEABLE Na	SODIUM RELEASE			ORIGINAL REPLACEABLE K	POTASSIUM RELEASE			
				Original	Final		60 days	180 days	360 days		Initial*	60 days	180 days	360 days
			inches			*me.*†	*me.*	*me.*	*me.*	*me.*	*me.*	*me.*	*me.*	*me.*
P-80-2	Marshall	A	2 – 5	3.8	4.5	0.05	0.04	0.06	0.12	1.94	0.08	0.12	0.16	0.21
P-80-7		B	18 –22	4.0	5.1	0.12	0.03	0.03	0.05	0.61	0.08	0.12	0.08	0.10
P-80-14		C	54 –60	4.2	5.1	0.18	0.07	0.08	0.17	0.50	0.09	0.13	0.13	0.18
P-124-2	Sharpsburg	A	3 – 6	—	4.5	0.05	0.06	0.12	0.18	0.84	0.13	0.15	0.21	0.23
P-124-4		A-B	9 –12	—	4.1	0.07	0.12	0.19	0.30	0.55	0.12	0.15	0.16	0.17
P-124-7		B	18 –21	—	3.9	0.10	0.14	0.26	0.35	0.58	0.12	0.13	0.13	0.15
P-376-1	Haig	A	0 – 6	3.8	4.6	0.03	0.05	0.09	0.17	0.54	0.07	0.17	0.25	0.25
P-376-3		A-B	10 –12	4.1	4.5	0.04	0.07	0.10	0.12	1.01	0.06	0.08	0.09	0.12
P-376-5		B	22 –28	4.4	5.0	0.15	0.05	0.09	0.09	0.78	0.06	0.09	0.10	0.12
P-76-2	Seymour	A	4 – 8	4.0	4.5	0.07	0.05	0.10	0.12	0.67	0.06	0.06	0.09	0.12
P-76-3		A-B	8 –11	4.0	4.4	0.07	0.07	0.12	0.14	0.46	0.06	0.05	0.07	0.08
P-76-7		B	18 –21	4.3	4.3	0.47	0.08	0.24	0.24	0.51	0.05	0.12	0.12	0.13
P-377-1	Edina	A	0 – 5	3.7	4.1	0.04	0.11	0.16	0.24	0.63	0.04	0.09	0.10	0.15
P-377-3		A_2	10 –15	4.1	4.4	0.11	0.05	0.12	0.18	0.34	0.04	0.07	0.03	0.08
P-377-6		B	20 –25	4.4	4.9	0.63	0.07	0.08	0.09	0.23	0.05	0.08	0.06	0.10
P-139-1	Taintor	A	0 – 6	—	4.4	0.09	0.08	0.21	0.25	0.48	0.11	0.12	0.15	0.15
P-139-3		A-B	9 –12	—	4.0	0.11	0.13	0.24	0.29	0.32	0.09	0.09	0.09	0.12
P-139-7		B	21 –24	—	4.6	0.12	0.11	0.16	0.21	0.29	0.06	0.09	0.09	0.12
P-101-2	Fayette	A	1 – 3	4.0	4.3	0.05	0.06	0.11	0.15	0.21	0.01	0.03	0.06	0.10
P-101-4		A-B	6 – 8	3.9	4.0	0.07	0.07	0.10	0.10	0.23	0.02	0.04	0.05	0.08
P-101-6		B	10 –12	4.0	4.0	0.10	0.09	0.13	0.24	0.29	0.03	0.08	0.09	0.13
P-119-1	Fayette	A	0 – 3.5	—	4.6	0.03	0.10	0.21	0.23	0.70	0.06	0.11	0.23	0.23
P-119-6		A-B	16 –19	—	4.2	0.10	0.10	0.12	0.14	0.38	0.05	0.09	0.10	0.10
P-119-10		B	29.5–33.5	—	4.1	0.08	0.09	0.19	0.28	0.40	0.07	0.08	0.15	0.14
P-4-2	Weller	A	1.5– 4	4.0	4.4	0.09	0.06	0.17	0.17	0.27	0.03	0.08	0.16	0.17
P-4-4		A_2	6 – 8	4.2	4.7	0.12	0.05	0.18	0.18	0.34	0.03	0.08	0.11	0.12
P-4-8		B_1	16 –19	3.9	3.5	0.22	0.06	0.07	0.14	0.53	0.04	0.04	0.11	0.12
P-7-2	Marion	A	0 – 3	4.1	4.5	0.03	0.06	0.11	0.13	1.94	0.03	0.08	0.13	0.13
P-7-6		A_2	10 –12	4.1	4.6	0.12	0.08	0.10	0.10	0.61	0.02	0.03	0.02	0.06
P-7-9		B	18 –21	4.0	4.8	1.21	0.03	0.07	0.10	0.50	0.04	0.05	0.07	0.09
P-116-1	Webster	A	0 – 5	4.6	4.9	0.10	0.08	0.17	0.18	0.53	0.10	0.09	0.07	0.12
P-116-4		A-B	15 –19	4.3	4.6	0.13	0.08	0.14	0.14	0.47	0.06	0.07	0.09	0.11
P-116-6		B	23 –28	4.6	4.4	0.12	0.10	0.09	0.22	0.33	0.09	0.09	0.08	0.10
P-114-1	Carrington	A	0 – 6	—	4.1	0.04	0.06	0.19	0.22	0.25	0.07	0.06	0.09	0.10
P-114-5		A-B	17 –21	—	4.4	0.08	0.08	0.08	0.13	0.18	0.04	0.03	0.02	0.03
P-114-7		B	26 –31	—	4.2	0.09	0.07	0.11	0.14	0.27	0.04	0.03	0.04	0.05
P-117-1	Floyd	A	0 – 5	3.8	4.1	0.11	0.08	0.11	0.17	0.25	0.04	0.05	0.06	0.08
P-117-3		A-B	10 –15	4.2	4.3	0.10	0.09	0.15	0.18	0.30	0.03	0.03	0.02	0.04
P-117-7		B	19 –23	4.5	4.7	0.11	0.06	0.07	0.07	0.34	0.04	0.04	0.03	0.06

* Amount released while the soils were drying following removal of all the original replaceable cations. No other bases were released during the period.

† me. = per 100 gm.

A relationship between soil parent material and K release is evidenced by the fact that the soils developed from glacial till or mixed till and loess showed a tendency to release less K than the soils developed entirely from loess. This is in agreement with the findings of Lawton.[3] No consistent differences in the rate of Na release between loess and till derived soils were apparent.

The best examples provided in this study for relating the degree of soil development to Na and K release are found in the group of soils from the loess traverse in southwest and southern Iowa. The ratios of Na released to K released in 1 year from these soils, arranged in order of increasing degree of horizon differentiation, are as follows: Marshall, 0.57; Sharpsburg, 0.78; Haig, 0.68; Seymour, 1.00; and Edina, 1.60. Thus there is some evidence of a trend toward a greater release of Na relative to K as the soils become more highly weathered.

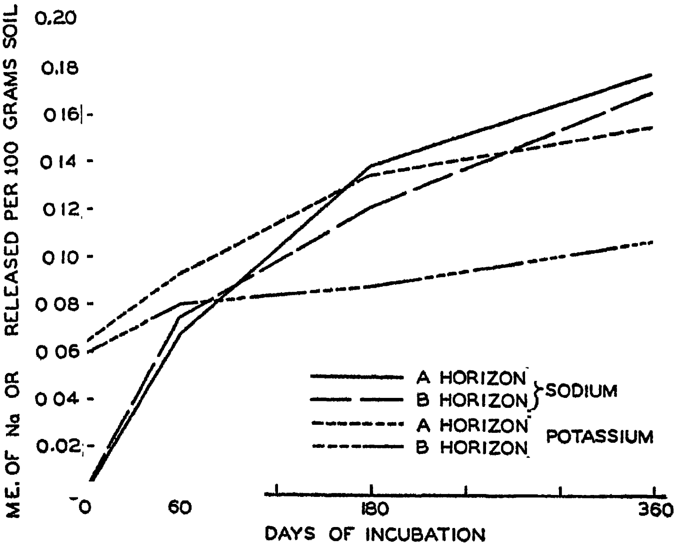

FIG. 1. AVERAGE RELEASE OF NA AND K FROM A AND B HORIZONS OF 13 SOILS DURING 360 DAYS' MOIST INCUBATION

DISCUSSION

The interpretation of the results of this investigation is based upon consideration of the Na and K minerals likely to be present in these soils, as well as upon what is known about the reactions of K in soils.

The primary minerals which contribute K to soils include a variety of micaceous minerals as well as several of the feldspars. Some of the micaceous minerals are probably of secondary origin or at least have been notably altered by soil-forming processes. In soils of this region the micaceous minerals, such as illites, tend to be more common in the fine silt and coarse clay fractions than in other separates. Hutton[4] found the 2–0.2μ clay from some of the soils studied here to be higher in total K than the coarser or finer fractions. It has also been well established by a number of investigators that soluble K is converted to difficultly replaceable forms upon contact with soil clays. The movement of K to and from the replaceable form in soils of the corn belt has been outlined by Wood and DeTurk (15). The replaceable K of soils tends to be in equilibrium with the nonreplaceable forms. Once this equilibrium is disturbed either by additions or removals of replaceable K, movements to or from the nonreplaceable forms tend to restore the equilibrium level in the replaceable form. Attoe (1) has pointed out that the shift toward equilibrium is particularly rapid when the soil is dried. This was evidenced in these studies by the large amounts of K released when the leached samples were dried.

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[3] Lawton, K. Unpublished data. Iowa Agr. Exp. Sta.

[4] Hutton, C. E. The morphology and genesis of prairie soils developed from Peorian loess in southwestern Iowa. 1948. [Unpublished Ph.D. thesis. Copy on file Iowa State Col-

Another factor in the K cycle is that plants growing on the soil tend to enrich the surface soil in K at the expense of layers immediately below the surface. Therefore, although the amounts of replaceable K and the rate of K release slowly decline as the soil loses K by leaching, the surface soil tends to lie behind the layers immediately beneath it in the extent of this decline.

In contrast to the situation with K, the feldspar group of minerals would be the only source of most of the Na released in these soils, Furthermore, the Na feldspars are not likely to be found in the finer size fractions of soils of this region. For example, Hutton (6) found that the Na contents of clay fractions isolated from some of the soils studied here were very low. It has also been pointed out by Jackson *et al.* (7) that the presence of albite as a major constituent of the clay fraction is to be expected only in soils of a somewhat less advanced stage of weathering than those studied here. Most of the Na released in these soils, therefore, probably originated from silt-sized particles. Once activated by decomposition of the feldspar minerals, the Na would remain in replaceable or water-soluble forms until leached out of the soil or removed by crops, since Na is not a common constituent of secondary minerals, nor is it appreciably fixed in difficultly replaceable form by the clay fraction of soils (8).

Since the surface soils studied here tended to release more Na than was originally present in the untreated soils, it seems unlikely that the original replaceable Na content represented an equilibrium controlled by the solubility of the Na-feldspars. The fact that Na release was continuing even at the later stages of the release experiment also indicates that an equilibrium level was not being approached. It does not appear that the solubility of the Na-feldspars was greatly increased by saturation of the soils with H^+, since a few preliminary trials indicated that Ca^{++}-saturated soils released at least as much Na as did the same soils when saturated with H^+. Another significant point is that, among the soils considered here, the highest amounts of replaceable Na were found in B horizons of soils in which leaching is restricted by the nature of the subsoil. A similar, although much greater, accumulation of Na in the B horizons of highly weathered claypan soils of Illinois has been reported by Smith (10).

It appears, then, that the amount of replaceable Na in these soils is the result of a balance between a slow but steady release of Na from the silt and the leaching loss of Na from the profile. The results of Stauffer (12) showing that rather large amounts of Na were leached out of lysimeters containing some similar soils are in accord with this point of view.

Within the limits of the degrees of soil weathering represented by the soils used here, there was no distinct trend in the rate of Na release with weathering. This may be because relatively coarse particles constitute the source of the Na released. Since the Na comes from coarser materials than the K, the positions of the Na minerals and the K minerals in weathering sequences such as proposed by Goldich (5) are reversed. This is in agreement with the observations of Jackson *et al.* (7) on the particle-size function in the weathering sequence.

TABLE 2

Replaceable sodium content of Iowa soils

SOILS	NUMBER OF SAMPLES	REPLACEABLE Na	
		Range	Average
		me./100 gm.	*me./100 gm.*
Developed from glacial drift			
Mankato			
Harpster	8	0.05 to 0.17	0.10
Webster	8	0.10 to 0.24	0.15
Clarion-Nicollett	2	0.07 to 0.13	0.11
Iowan			
Carrington-Floyd	5	0.04 to 0.11	0.09
Developed from loess			
Deep loess			
Marshall-Sharpsburg	8	0.05 to 0.27	0.13
Tama-Muscatine	4	0.09 to 0.22	0.16
Thin loess			
Grundy-Haig-Seymour-Edina	7	0.07 to 0.13	0.11
Fayette-Weller	2	0.03 to 0.09	0.06

In regard to the total amounts of Na and K released within 1 year, it must be kept in mind that the replaceable ions were allowed to accumulate in the soil for the entire period. Had the ions been removed from time to time during the experiment, K release might have increased relative to Na release.

Table 2 shows the results of a survey of the replaceable Na contents of the surface horizon of a large number of Iowa soils. The soils do not differ greatly in the amounts of replaceable Na, although the more highly leached soils tend to be low. The amounts of replaceable Na are in the same range as that found by other investigators (2, 10, 14) working with soils from the humid regions. On an average, about five times as much replaceable K as replaceable Na was present. Apparently, the equilibrium between release and leaching losses is rather constant in soils of this region, and thus the soils do not differ greatly in the amount of replaceable Na present.

SUMMARY

The amounts of replaceable Na and K and the rates of release of these two elements from nonreplaceable to replaceable forms in a number of Iowa soils have been studied. Samples from three horizons from 13 soil profiles were freed of replaceable bases, H+-saturated, and incubated at field capacity moisture contents. At the end of 60, 180, and 360 days, aliquots were removed and replaceable Na and K determined.

In general, more Na than K was released during 360 days of incubation. The range in amounts of Na released was from 0.05 to 0.35 me. per 100 gm. with an average of 0.17 me. The amounts of K released varied from 0.03 to 0.25 me. per 100 gm., with an average of 0.12 me. The soils originally contained averages of 0.09 and 0.50 me. of replaceable Na and K per 100 gm., respectively.

Significant amounts of K, but no Na, were released from nonreplaceable forms during the short period of drying of the acid-washed soils prior to incubation. The rate of release of Na was not greatly reduced with advanced time after removal of the replaceable bases. In contrast to Na release, the rate of release of K declined sharply during the later stages of the release experiment.

No consistent relationship between the amount of Na release from the A horizon and the degree of soil development was apparent in these studies.

The replaceable Na content of the A horizon of 42 soils studied showed a range of 0.03 to 0.27 me. per 100 gm., with an average of 0.13 me. The amount of replaceable Na in a soil appears to be the result of an equilibrium between a rather steady release from nonreplaceable forms and loss through leaching.

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SOME REACTIONS OF PHOSPHATE WITH CLAYS AND HYDROUS OXIDES OF IRON AND ALUMINUM

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Received for publication March 6, 1950

The many contemporary papers on the fixation of phosphate in the soil bespeak the importance of the phenomenon. Most soils rapidly convert the soluble phosphate of conventional fertilizers into relatively insoluble forms, thus immobilizing much of the phosphate in the region of its original placement and greatly decreasing its availability as a plant nutrient.

Of the various forms in which phosphorus may be held by the soil, the most significant appear to be certain calcium phosphates (1, 4, 10), exchangeable combinations with clay and hydrous oxides of iron and aluminum (11, 18, 23), and phosphates of iron and aluminum (6, 8, 13, 14, 15, 16, 20, 26). Despite a large number of investigations, however, the exact nature of the reactions of phosphorus with the soil constituents is poorly understood, presumably because of the difficulty with which the products of the fixation reactions are detected and identified in soil systems.

The present paper describes measurements of the rate of fixation of phosphorus by relatively pure preparations of individual clays and hydrous oxides of iron and aluminum under various conditions of temperature, pH, and concentration of phosphate. The paper also presents observations relative to the nature of the reactions of phosphate with the several soil minerals. In the following discussion the term "fixation" is used in a broad sense to indicate any reaction whereby phosphate is converted from a relatively soluble to a relatively insoluble form.

FIXATION EXPERIMENTS

Preparation of materials

Kaolinite, illite, and montmorillonite were separated as $< 0.3\text{-}\mu$ fractions by centrifuging dispersions of high-grade natural clays and were converted to the hydrogen form by electrodialysis. The montmorillonite was a sodium bentonite marketed by the American Colloid Company under the trade name *Volclay*. The illite was obtained from the Illinois State Geological Survey, and the kaolinite from the Georgia Kaolin Company. The hydrogen clays were not allowed to dry after the electrodialysis but were kept as 5 or 10 per cent aqueous suspensions until ready for use. The appearance of the clays in the electron microscope and their x-ray diffraction patterns indicated that they were relatively pure.

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Gibbsite was prepared by chemical precipitation. A < 2-μ fraction, separated by decantation from a dispersed suspension and dried at 50°C., was used for the tests. The separate gave a sharp x-ray diffraction pattern of gibbsite, $Al_2O_3 \cdot 3H_2O$.

TABLE 1

Composition of minerals used in phosphate-fixation studies

MINERAL	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	K_2O	MgO	CaO	IGNITION LOSS*
	%	%	%	%	%	%	%	%
Montmorillonite	55.5	20.0	3.8	0.03	0.13	2.8	1.1	14.3
Illite	49.4	25.4	6.9	0.31	6.0	2.3	0.05	8.2
Kaolinite	45.2	38.4	1.2	0.15	—	—	—	15.4
Gibbsite	0.1	65.4	0.1	0.03	—	—	—	31.7
Goethite	5.7	5.5	75.3	0.78	—	—	—	13.6

* Ignition temperature, 1,000°C.

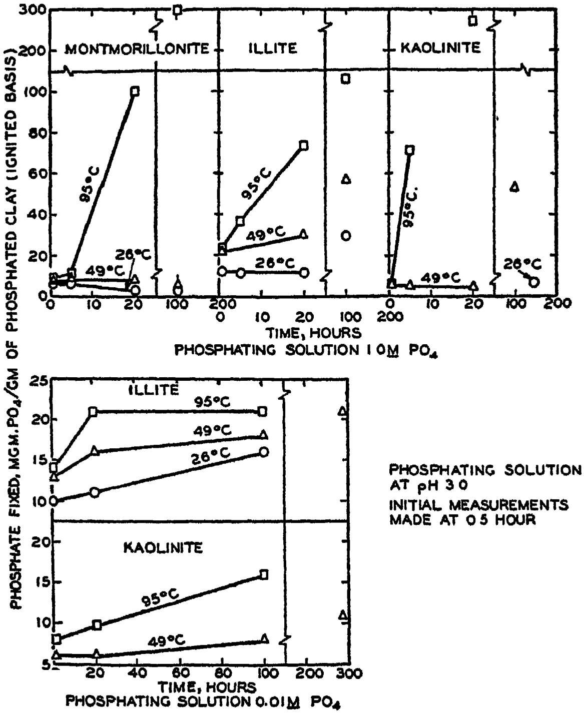

FIG. 1. EFFECT OF TEMPERATURE ON THE FIXATION OF PHOSPHATE BY CLAY MINERALS

Goethite, $Fe_2O_3 \cdot H_2O$, was prepared by wet-grinding selected specimens of the natural mineral with steel balls in a porcelain jar, recovering the < 2-μ fraction by decantation, and drying the product at 95° C.

The chemical composition of the clays and hydrous oxides is shown in table 1.

Rate of phosphate fixation

The rate at which the minerals fixed phosphate from aqueous solutions of potassium phosphate was measured at 26°, 50°, and 95°C. The solutions were prepared from potassium hydroxide and orthophosphoric acid; they were 0.01, 0.1, and 1.0 *M* with respect to phosphate and were at pH's of 3, 5, and 7.

A 2-gm. charge of mineral was dispersed in 25 ml. of water in a 250-ml. centrifuge bottle, and 200 ml. of a phosphate solution was added. The sample was kept in a constant-temperature bath for a predetermined period and was shaken by hand at frequent intervals. Solid and solution then were separated by centrifugation and decantation. The solid was washed centrifugally in successive 200-ml. portions of aqueous ethyl alcohol. Because of the insolubility of potassium phosphate in alcohol, the alcohol content of the wash solutions was adjusted to the salt content of the sample. When the phosphating solution was 1.0 *M*, the solid was washed once with 20 per cent, once with 50 per cent, and then several times with 80 per cent alcohol. When the phosphating solution was 0.1 or 0.01 *M*, the solid was washed once with 50 per cent and then repeatedly with 80 per cent alcohol. Five washes generally proved ample.

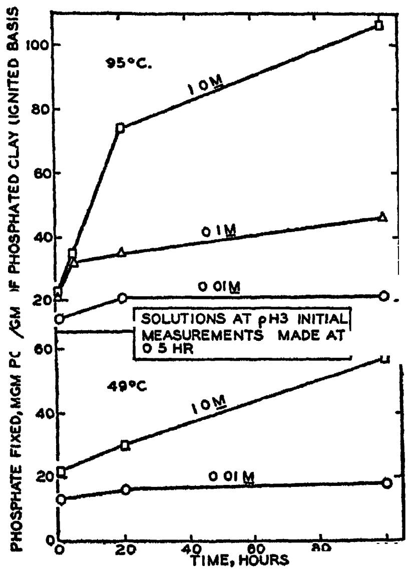

Fig. 2. Fixation of Phosphate by Illite as a Function of the PO$_4$ Content of the Phosphating Solution

The fixed phosphate was determined by chemical analysis of the treated minerals. The results, as computed on the basis of the treated minerals after ignition, are plotted to show the relative rates of fixation in figures 1 to 5. All the minerals showed an initial rapid rate of reaction with phosphate in the period from 0 to 0.5 hour and a subsequent slower rate. This phenomenon has been observed by other investigators and is indicative either of two mechanisms of fixation or of two manifestations of the same mechanism.

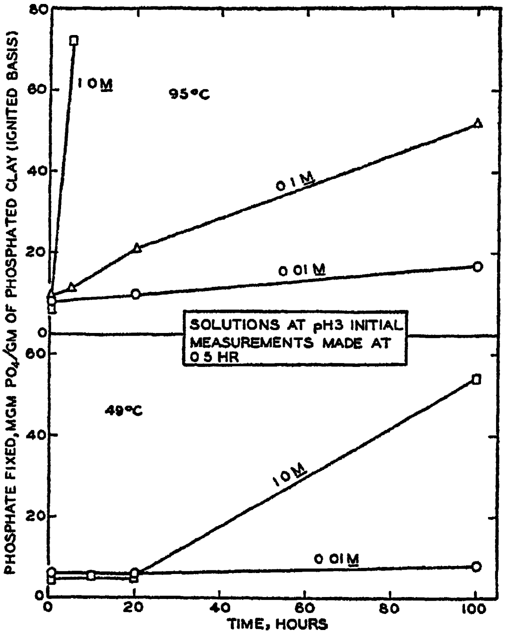

FIG 3 FIXATION OF PHOSPHATE BY KAOLINITE AS A FUNCTION OF THE PO$_4$ CONTENT OF THE PHOSPHATING SOLUTION

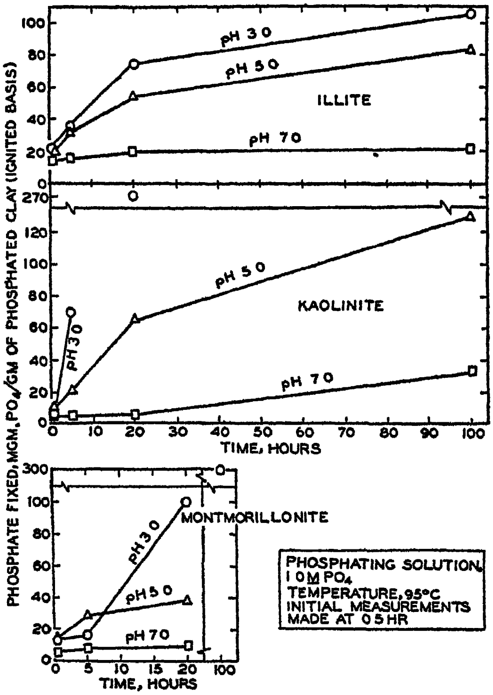

FIG. 4. EFFECT OF pH ON THE FIXATION OF PHOSPHATE BY CLAY MINERALS

The rate of fixation by the clay minerals increased with rise in the temperature (fig. 1), with increase in the concentration of solute phosphate (figs. 2 and 3), and with lowering in the pH (fig. 4). As shown in figure 5, the rate of fixation by the hydrous oxides also increased somewhat with increase in the temperature but was relatively rapid even at 26°C., whereas the pH had little effect. In general, the decreasing order in which the minerals fixed phosphate under the experimental conditions was: gibbsite, goethite, illite, kaolinite, montmorillonite, the rate for gibbsite being much higher than for the others. The clays were variable, however, in their relative reaction rates at high temperatures and high concentrations of phosphate.

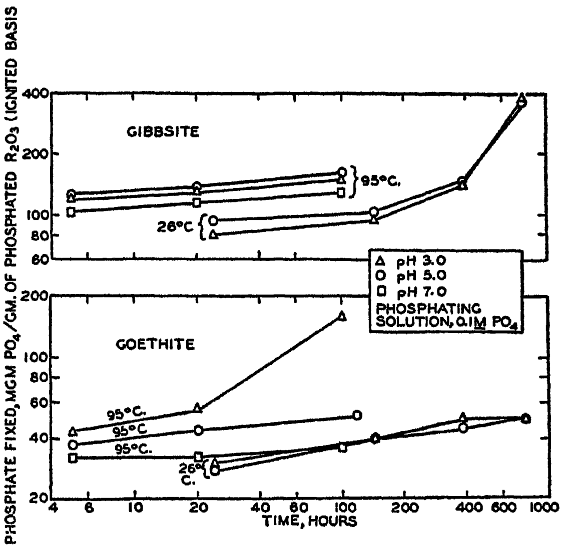

FIG. 5. EFFECTS OF TEMPERATURE AND pH ON THE FIXATION OF PHOSPHATE BY GIBBSITE AND GOETHITE

Some of the clays that had fixed high proportions of phosphate were found by microscopic examination to contain distinct hexagonal-shaped crystals. A concentrate of the crystals, separated by sedimentation from a phosphate-treated illite, was subjected to x-ray diffraction analysis. The interplanar spacings were similar to those of palmerite (2). Dana (9) gives the composition of palmerite as $HK_2Al_2(PO_4)_3 \cdot 7H_2O$. Palmeritelike crystals also were identified microscopically in clays that had been alternately wetted with phosphate solution at pH 3 to 5 and dried at room temperature.

The detection of these crystalline products of the treatment of clays with phosphate, together with the possibility that such products might reflect a mechanism of phosphate fixation in the soil, prompted a study of substituted forms of palmerite.

PREPARATION AND PROPERTIES OF SUBSTITUTED PALMERITES

Reference to the observation of palmeritelike minerals in the soil or in phosphate-fixation tests was not found in the literature. Bannister and Hutchinson

(3) reported, however, that soil conditions sometimes are favorable for the formation of palmerite and suggested that it may be one of the forms in which phosphate becomes fixed in the soil. Murphy (22) and Stout (25) reported experiments in which the structure of clays of the kaolinite group was altered by phosphation. Both Murphy and Stout ground their clays severely in a ball mill, a treatment likely disruptive to the clay lattice (19, 21, 24), and the structural alteration observed by them may have been influenced by the grinding. The x-ray pattern reported by Stout for phosphated halloysite is similar to that of palmerite.

Ford (13) concluded from phosphate-fixation tests with gibbsite and goethite that crystalline aluminum and iron phosphates were formed, although he could not establish the specific mineral species from x-ray patterns. Unfortunately he did not report the diffraction lines.

Ensminger (12) recently showed that ammonium aluminum phosphates, appearing crystalline on examination by x-ray diffraction, are produced by the reaction of ammonium phosphate with kaolinite, aluminum oxide, and soil colloids. Similar ammonium aluminum phosphates were produced by mixing solutions of aluminum chloride and ammonium phosphate. Ensminger did not identify his compounds, but they probably were palmeritelike products.

Palmerites from the treatment of soil minerals with phosphate.

The preparation of substituted palmerites in relatively pure form was attempted by phosphate treatment of the clays, montmorillonite, illite, and kaolinite, as well as the hydrous iron oxides, goethite and limonite. The < 0.3-μ hydrogen clays and the < 2-μ goethite were those described in a preceding section. The limonite was a specimen of relatively pure bog limonite that was ground to $< 2\ \mu$.

The phosphating solutions were ammonium, potassium, and sodium phosphates, 1.0 *M* with respect to PO_4 and at pH 3.0 or 5.0, as well as magnesium and calcium phosphates, 0.1 *M* with respect to PO_4 and at pH 3.0. The solutions were prepared by addition of the respective hydroxides to phosphoric acid.

A 10- or 20-gm. charge of a given mineral was treated at 95°C. for three 5-day periods with successive 500-ml. portions of a phosphating solution.

Abundant crystals, 2 to 20 μ, were formed when the clays were treated with alkali or ammonium phosphates. The crystals were washed and separated in relatively pure form by dispersing the solids repeatedly in distilled water and decanting off the fine clay and silica. The goethite and limonite also produced crystalline phosphates of relatively large size, but the phosphate crystals generally contained many inclusions of unreacted oxide.

The products from most of the treatments with calcium and magnesium phosphates were contaminated with dicalcium or dimagnesium phosphate, and identification of the aluminum iron phosphate phase was uncertain. From a few of the magnesium phosphate treatments, however, relatively pure crystalline aluminum iron phosphates were isolated. Microscopic examination indicated that the aluminum iron phosphates produced in the calcium phosphate treatments were of the same crystal form as those produced in the magnesium phosphate treatments.

The chemical composition of the washed crystalline phosphates is shown in table 2. The data of table 3 were obtained from x-ray diffraction patterns, and figure 6 shows photomicrographs of typical crystalline products.

TABLE 2

Chemical composition of crystalline products of the treatment of clays and hydrous iron oxides with phosphate

PHOSPHATING SOLUTION	SOIL MINERAL	ADDED BASE	Al_2O_3	Fe_2O_3	P_2O_5	SiO_2	IGNITION LOSS*	PRODUCT NO.
		%	%	%	%	%	%	
Ammonium phosphate†	Montmorillonite	4.4 NH_4	28.0	5.1	42.5	3.3	22.3	1
	Illite	5.5	23.7	6.8	40.2	8.3	21.0	2
	Kaolinite	5.7	29.0	0.9	45.0	1.5	24.5	3
	Goethite	4.0	3.5	59.3	17.8	2.5	14.9	4§
Potassium phosphate‡	Montmorillonite	10.3 K_2O	16.5	3.0	39.6	9.6	21.0	5
	Illite	10.8	18.3	6.3	43.7	0.8	22.3	6
	Kaolinite	11.2	20.4	0.9	44.8	1.3	22.0	7
	Kaolinite	12.9	25.6	0.6	35.6	9.7	15.9	8
	Goethite	10.6		44.3	31.9		12.1	9
	Limonite	11.6		39.8	34.8		12.6	10
Sodium phosphate†	Illite	10.3 Na_2O	17.5	6.0	48.5	1.5	17.0	11
	Kaolinite	8.5	23.8	0.7	49.2	2.0	15.0	12
	Goethite	3.7	3.8	54.5	18.3	3.3	14.3	13§
Magnesium phosphate†	Illite	tr. MgO	26.1	8.5	40.8	5.3	18.9	14
	Kaolinite	0.8	31.2	0.6	40.0	21.6	6.0‖	15
	Goethite	0.9	0.9	69.6	8.5	4.0	14.5	16§

* Ignition temperature, 1,000°C.

† Solution at pH 3.

‡ Solution at pH 5 for kaolinite product 8; at pH 3 for others in group.

§ Product contained much unreacted goethite.

‖ Low ignition loss attributable to high drying temperature (175°C.).

The over-all findings from the chemical analyses, x-ray analyses, and optical studies indicate that the products resultant from treatment of the soil minerals with phosphates of ammonium, potassium, and sodium were members of an isomorphous series of aluminum iron phosphates with the general composition, $[(H, Na, K, NH_4)_3, Fe, Al]PO_4 \cdot nH_2O$, where Fe plus Al is greater than 0 but less than 1. The x-ray patterns of these minerals were similar to that of palmerite with some spreading and shifting of lines, presumably because of cation substitutions or differences in water of hydration.

The products produced with magnesium phosphate gave x-ray diffraction paterns almost identical with that of barrandite (2). This identification was verified by the chemical composition and optical properites of the compounds, and it is concluded that these preparations were members of the variscite ($AlPO_4 \cdot 2H_2O$), barrandite (Al, Fe)$PO_4 \cdot 2H_2O$, strengite ($FePO_4 \cdot 2H_2O$) isomorphous series.

TABLE 3

X-ray diffraction patterns of crystalline products of the treatment of clays and limonite with phosphate

PALMERITE, A.S.T.M. (2)		PHOSPHATED PRODUCTS AS NUMBERED IN LAST COLUMN OF TABLE 2*											
		6		5		8		3		12		10	
d	Intensity	*d*	Intensity†	*d*	Intensity†	*d*	Intensity†	*d*	Intensity†	*d*	Intensity†	*d*	Intensity†
A.		*A.*		*A.*		*A.*		*A.*		*A.*		*A.*	
15.5	1.0	15.7	VS	14.1	S								
										8.9	VS		
		7.9	MW										
7.6	0.8	7.4	M	7.4	M			7.5	MW	7.7	S	7.1	VW
				6.95	W	6.8	S	6.7	VS			6.7	S
				6.52	VW								
5.8	0.6	5.8	M					5.8	VS	5.8	W	5.9	S
				5.57	M	5.5	S						
5.1	0.2	5.03	MW			4.9	W			5.14	VW		
4.72	0.4	4.67	VW			4.6	VW	4.61	M	4.76	MW	4.7	W
										4.48	W		
4.39	0.6	4.31	M	4.34	M	4.3	VW	4.27	W	4.28	MW	4.2	W
				4.15	MW	4.15	W	4.13	MW	4.15	W		
		4.02	W			4.07	VW			3.88	W	4.04	W
3.82	0.8	3.78	MS					3.70	MW	3.75	S		
3.58	0.6	3.56	M	3.68	W	3.64	VW			3.64	W	3.63	W
				3.42	S	3.39	W						
3.34	0.5	3.33	W			3.34	W	3.32	W			3.35	W
		3.28	W			3.22	MW			3.22	MW		
3.15	0.8	3.12	MS	3.16	MW	3.15	MW						
				3.04	W	3.07	W	3.00	MS	3.04	VS	3.04	S
2.95	0.8	2.90	M	2.90	W	2.91	MW	2.94	MS			2.98	MS
2.84	0.8	2.81	M	2.79	MW	2.78	MW	2.80	MS	2.86	W	2.82	MS
2.73	0.2	2.71	MW										
2.63	0.7	2.62	MS	2.66	W			2.62	S	2.63	MW	2.65	MW

* Radiation, Cu $K\alpha$; camera diameter, 14.32 cm.

† VS, very strong; S, strong; MS, medium strong; M, medium; MW, medium weak; W, weak; VW, very weak.

Most of the crystalline phosphates were of sufficient purity to afford an approximation of their empirical formulas by means of their chemical analyses, particularly since the microscope showed that only one phosphate phase was present in a given sample and that the impurities were mostly silica and undecomposed parent minerals. Table 4 lists such formulas; they were calculated on the assumptions that (*a*) the silica was either free or present as unreacted mineral, (*b*) any excess aluminum or iron was present as unreacted mineral, (*c*) the water was equal to the ignition loss or to the ignition loss minus the ammonia, and (*d*) when necessary, hydrogen should be included in the formula to balance excess phosphate, such hydrogen being subtracted from the water of hydration.

The optical properties of the crystalline phosphates varied somewhat with cation substitutions in the lattice. Increases in the iron in the lattice caused increases in the indexes of refraction, birefringence, and optic angle of the crystals, and the products became lemon-yellow or greenish yellow. With substitution of ammonium for potassium plus hydrogen, or for sodium plus hydrogen, the crystal symmetry shifted from orthorhombic to monoclinic. Often the indexes of refraction and color of crystals within the same product varied appreciably, although the crystal form was homogeneous. The increases in the intermediate index of refraction and the birefringence of the various compounds, as affected by increase in iron content, are shown in a general way through the following tabulation:

TABLE 4

Empirical formulas for products of the treatment of clays and hydrous iron oxides with phosphate

DUCT NO.*	EMPIRICAL FORMULA
	$(NH_4)_{1.2}Al_{2.3}Fe_{0.3}(PO_4)_3 \cdot 5.0H_2O$
	$(NH_4)_{1.7}Al_{1.9}Fe_{0.5}(PO_4)_3 \cdot 4.7H_2O$
	$(NH_4)_{1.5}Al_{2.4}Fe_{0.1}(PO_4)_3 \cdot 5.0H_2O$
5	$H_{1.8}K_{1.2}Al_{1.8}Fe_{0.2}(PO_4)_3 \cdot 5.4H_2O$
6	$H_{1.3}K_{1.1}Al_{1.8}Fe_{0.4}(PO_4)_3 \cdot 5.4H_2O$
7	$H_{1.9}K_{1.1}Al_{1.9}Fe_{0.1}(PO_4)_3 \cdot 4.8H_2O$
8	$K_{1.7}Al_{2.4}Fe_{0.04}(PO_4)_3 \cdot 5.3H_2O$
9	$K_{1.5}Fe_{2.5}(PO_4)_3 \cdot 4.5H_2O$
10	$K_{1.5}Fe_{2.5}(PO_4)_3 \cdot 4.3H_2O$
11	$H_{2.1}Na_{1.5}Al_{1.5}Fe_{0.3}(PO_4)_3 \cdot 3.2H_2O$
12	$H_{1.7}Na_{1.2}Al_{2.0}Fe_{0.04}(PO_4)_3 \cdot 2.7H_2O$
14	$(Al_{0.8}Fe_{0.2})PO_4 \cdot 1.8H_2O$
15	$(Al_{0.99}Fe_{0.01})PO_4 \cdot 0.6H_2O$†

* As listed in last column of table 2.

† Low value for water of hydration attributable to drying at 175°C. prior to determination of ignition loss.

MONOVALENT BASE PRESENT	PHOSPHATE HIGH IN Al		PHOSPHATE HIGH IN Fe	
	β	Birefringence	β	Birefringence
NH_4	1.566	0.008	1.660	0.020
Na	1.540	0.008	1.648	0.050
K	1.540	0.010	1.620	0.045

The pH of the phosphating solution appeared to have some influence on the crystal habit of the product. In potassium phosphate solutions at pH 3, for example, pseudohexagonal, tabular crystals similar to kaolinite were formed, whereas in potassium phosphate at pH 5, prismatic crystals were formed (E and F, fig. 6).

With sodium phosphate at pH 3.0, pseudohexagonal crystals similar to those produced with potassium phosphate at the same pH were formed (A and B, fig. 6). On the other hand, ammonium phosphate always gave prismatic crystals with frequent staurolitic twins (C, fig. 6). The crystalline phosphates produced from limonite and goethite were poorly formed, highly twinned, and were always prismatic (D, fig. 6).

Precipitated palmerites

In view of the results obtained by phosphate treatment of the clays and hydrous oxides of iron and aluminium, it seemed likely that products with a palmerite structure might be formed by direct precipitation of iron and aluminum phosphates from solutions containing the monovalent ions Na^+, K^+, and NH_4^+.

Ten-gram charges of goethite and gibbsite were dissolved in boiling concentrated phosphoric acid or a mixture of this acid and sulfuric acid. The solutions were diluted to 100 ml., filtered, and further diluted to about 400 ml. To the boiling filtrates, solutions of potassium or ammonium hydroxide or suspensions of calcium or magnesium oxide were added slowly until a heavy precipitate was formed. In another experiment, 10 gm. of gibbsite was dissolved in a boiling solution of 30 gm. of potassium hydroxide in 50 gm. of water. The solution, diluted to 400 ml., was heated to boiling, and dilute phosphoric acid was added slowly until a heavy precipitate was formed. The final pH of each mother liquor was determined. The precipitates were washed with water, analyzed chemically, and their x-ray diffraction patterns determined. The results are summarized in table 5.

Products 17 and 18 (table 5) appeared to be potassium palmerites, and their x-ray patterns were almost identical with those of the products obtained through potassium phosphate treatment of clays. In products 19 and 20, ammonium was substituted for potassium, and the products still showed the characteristic pattern of palmerite, the precipitates varying in composition with the relative concentration of the ions in the substrate.

Product 23 (table 5), which was obtained by addition of calcium oxide to an aluminum phosphate solution, appeared amorphous in an x-ray examination, but its calcium content suggests that it may have been a calcium aluminum phosphate. Product 22, which resulted from the addition of magnesium oxide to an aluminum phosphate solution, was a hydrous aluminum phosphate similar in composition to that produced by treatment of clay with magnesium phosphate.

It appears that substitution of either ammonium or potassium for only a small fraction of the aluminum in aluminum phosphate is sufficient to yield a product characterized by a palmerite structure. It is possible, however, that the precipitates that were low in potassium and ammonium were mixtures of a palmeritelike material and an amorphous aluminum phosphate.

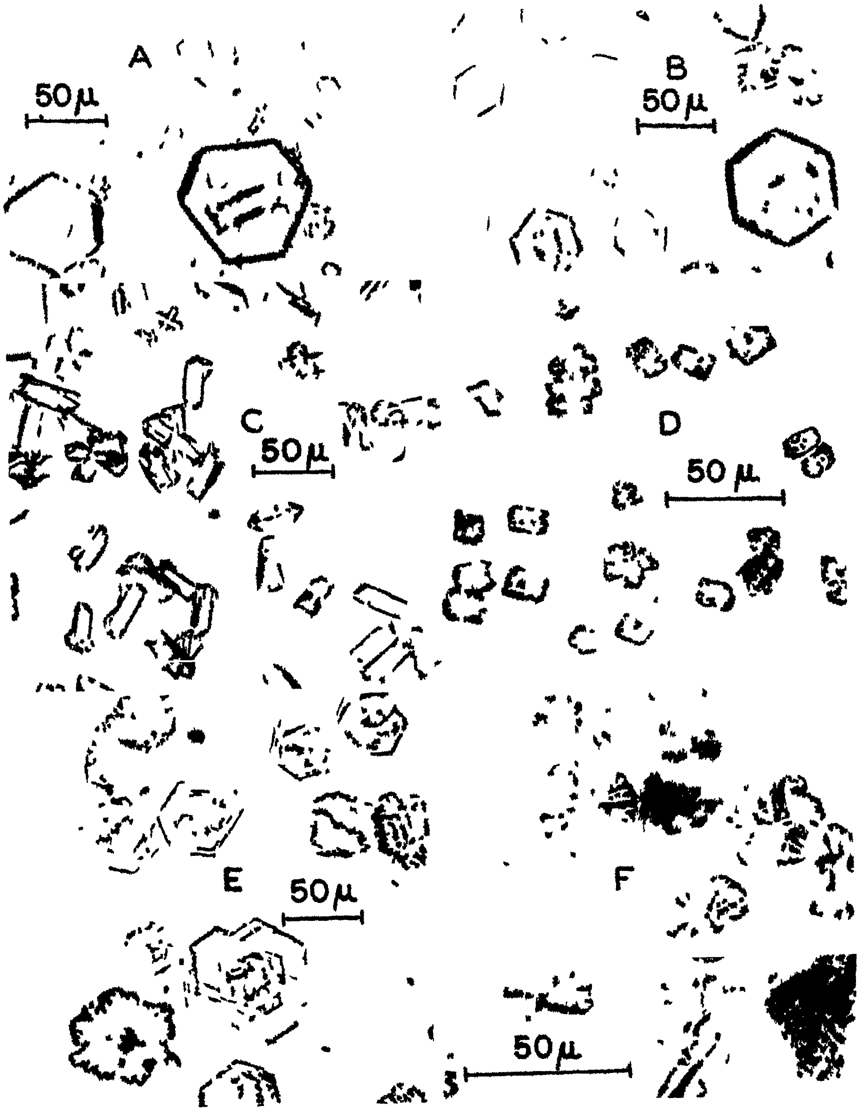

FIG 6 PHOTOMICROGRAPHS OF CRYSTALLINE PRODUCTS OF THE PHOSPHATION OF CLAYS AND LIMONITE

A, potassium palmerite from illite (product 6) B sodium palmerite from illite (product 11), C ammonium palmerite from kaolinite (product 3), D potassium palmerite from limonite (product 10), E potassium palmerite from kaolinite pH 3 (product 7), F, potassium palmerite from kaolinite, pH 5 (product 8) Product numbers refer to last column of table 2

Cole and Jackson (7) recently prepared iron and aluminum phosphates by mixing solutions of sodium hydroxide with slightly acid solutions of iron or aluminum chloride containing an excess of phosphate as potassium or sodium phosphate. The resulting compounds appeared amorphous when subjected to x-ray examination but gave definite electron diffraction patterns. When the fresh precipitates were digested at 70° to 100°C., the size of the crystals increased without a change in crystal species, and the compounds then gave sharp x-ray diffraction patterns. Cole and Jackson concluded that variscite and sterretite were present in the aluminum phosphate precipitates and that strengite was present in the iron phosphate preparations. The diffraction pattern of the compound they identified as sterretite is the same as that shown by product 8 in table 3 of the present report. Apparently palmeritelike compounds were present in some of the precipitates of Cole and Jackson. This conclusion is further supported by the electron photomicrographs of some of the preparations of Cole and Jackson which show tabular hexagonal-shaped crystals very similar to the sodium and potassium palmerites shown in figure 6 (A, B, and E).

TABLE 5

Chemical composition and x-ray diffraction patterns of iron and aluminum phosphates precipitated in the presence of the ions NH_4^+, K^+, Ca^{++}, and Mg^{++}

MINERAL DISSOLVED (10 gm.)	SOLVENT		PRECIPITANT	FINAL pH	PERCENTAGE COMPOSITION OF PRECIPITATE						TYPE X-RAY PATTERN	PRODUCT NO.
	Composition*	Weight			NH_4	K_2O	Al_2O_3	Fe_2O_3	P_2O_5	Ignition loss†		
		gm.										
Gibbsite	H_2SO_4 H_3PO_4	57 46	KOH	1.4		11.0	20.8		43.4	24.8	Palmerite	17
	H_2SO_4 H_3PO_4	20 15	KOH	1.8		6.7	22.6		35.2	34.9	Palmerite	18
	H_2SO_4 H_3PO_4	25 20	NH_4OH KOH	2.2	0.8	5.5	21.3		37.0	36.2	Palmerite	19
	H_2SO_4 H_3PO_4	25 20	NH_4OH	2.6	1.8		27.8		43.1	28.2	Palmerite	20
	KOH	80	H_3PO_4	8.4		17.4	28.2		37.8	15.7	Amorphous	21
	H_2SO_4 H_3PO_4	25 20	MgO	3.8	0.0 (MgO)		34.0		46.4	17.2	Very weak	22
	H_3PO_4	50	CaO	2.1	4.6 (CaO)		25.6		48.1	20.2	Amorphous	23
Goethite	H_2SO_4 H_3PO_4	48 10	KOH	0.8		3.5	0.7	39.0	34.4	19.1	Amorphous	24
	H_2SO_4 H_3PO_4	10 43	KOH	6.1		14.1	0.1	27.6	43.3	13.2	Very weak	25

* H_2SO_4, 90 per cent solution; H_3PO_4, 80 per cent solution; KOH, 38 per cent solution

† Ignition temperature, 1,000°C.

Solubilities of palmerites

Rough solubility measurements on several of the ammonium aluminum and potassium aluminum palmerites showed that they were nearly insoluble (2 to

4 ppm.) in distilled water and in Truog's reagent (27) for measurement of the readily available phosphorus in soils, that they were moderately soluble (100 to 500 ppm.) in a 1 per cent solution of ammonium hydroxide and in neutral 0.5 *M* ammonium fluoride, and that they were very soluble in a 1 per cent solution of sodium hydroxide. Qualitatively, the iron palmerites appeared to be less soluble than the aluminum palmerites.

RELATION OF PRESENT OBSERVATIONS TO MECHANISM OF PHOSPHATE FIXATION

The results of the present fixation experiments agree with those reported by other investigators in that they show two stages of phosphate fixation, a rapid initial reaction and a subsequent relatively slow reaction. Black (5) attributed the slow fixation to a gradual penetration of phosphate into the mineral lattice with a resultant replacement of internal hydroxyl ions. Later, however, he and Low (20) indicated that the slow fixation may be due to a decomposition of clays by phosphate in the soil solution with a resultant precipitation of iron and aluminum phosphates. The present results support Low and Black's view of the mechanism of the slow fixation.

The rapid initial fixation has been attributed by Dean and Rubins (11), by Kelly and Midgley (18), and by Ravikovitch (23) to an exchange of phosphate ions in the solution for hydroxyl ions on the surfaces of the mineral particles. A further insight into the mechanism of the rapid fixation is given in experiments reported by Wood and DeTurk (28) and by Hoover (17). These authors showed that both the exchangeable potassium and the fixed potassium were greater in soils that had been treated with potassium phosphate than in those treated with potassium chloride, and similar observations have been made in unreported experiments by the present authors.

It appears, therefore, that compounds chemically similar to palmerite may form during the initial stage of phosphate fixation in acidic soils that contain potassium, ammonium, or sodium, together with phosphate. Also, compounds similar chemically to variscite or strengite may form during the initial stage of phosphate fixation in acidic soils that have a very low concentration of these monovalent cations. Thus, the rapid rates and the slow rates of fixation probably reflect the same general type of chemical reaction.

The rapid fixation is believed to result from a combination of phosphate ions with superficial ions of aluminum and iron that are held in the extremities of the lattice or by exchangeable attachment on both the clays and the hydrous oxides of iron and aluminum. The product of this reaction initially is relatively soluble and presumably is readily available to plants, but its solubility decreases gradually, probably as a result of crystallization and partial dehydration to form phosphates similar to palmerite, variscite, or strengite. The escape of such products of the fixation reactions from detection in natural soils is believed to result from the extreme smallness of the crystals that likely are formed through the preponderantly superficial type of fixation that occurs at the low concentrations of phosphate normally present in soils. Furthermore, palmeritelike phosphates are difficult to distinguish from such clay minerals as kaolinite, halloysite, and nontronite by either optical or electron microscopy.

SUMMARY

Phosphate-fixation experiments were made on the minerals montmorillonite, illite, kaolinite, gibbsite, and goethite at temperatures of 26°, 49°, and 95° C., at pH's of 3, 5, and 7, and at 1.0, 0.1, and 0.01 *M* concentrations of phosphate. All the minerals were characterized by two stages of fixation, one progressing at a rapid rate and one at a much slower rate. It was concluded that both stages of fixation probably proceed through the same chemical reaction, that the rapid fixation results from the reaction of phosphate with readily available aluminum and iron, and that the slow fixation results from the reaction of phosphate with aluminum and iron that are released through decomposition of the respective minerals.

The rate of fixation by the clays, montmorillonite, illite, and kaolinite, increased with rise in temperature, with increase in concentration of phosphate, and with lowering in pH. The rate of fixation by the hydrous oxides, gibbsite and goethite, increased with rise in temperature but was affected little by variation in pH in the 0.1 *M* phosphate solutions. The decreasing order in which the minerals fixed phosphate generally was: gibbsite, goethite, illite, kaolinite, montmorillonite.

Complex iron and aluminum phosphates that showed x-ray diffraction patterns similar to the palmerite pattern were identified in some of the phosphate-treated clays. Relatively pure preparations of these phosphates were made by treatment of clays, limonite, and goethite with solutions of sodium, potassium, and ammonium phosphates. Chemical, microscopic, and x-ray analyses showed the compounds to be members of an isomorphous series with the general composition, $[(H, Na, K, NH_4)_3Fe, Al]PO_4 \cdot nH_2O$, where Fe plus Al is greater than 0 but less than 1. Crystalline phosphates of iron and aluminum were prepared through treatment of kaolinite and illite with magnesium phosphate and were found to be members of the variscite-barrandite-strengite isomorphous series. Phosphates similar to palmerite and variscite also were produced by precipitation from acidic solutions of aluminum and iron phosphates.

It is suggested that under some conditions phosphate may become fixed in the soil as substituted palmerites and as compounds in the variscite-barrandite-strengite isomorphous series. The escape of such crystalline products of the fixation reactions from detection in natural soils is attributed to the extremely small size of the crystals.

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REACTIONS OF PHOSPHATE WITH KAOLINITE

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Received for publication February 20, 1950

The reactions of phosphate with the sesquioxides of iron and aluminum, either by solution and chemical precipitation or by surface adsorption, have long been considered important factors in the fixation of phosphorus in acid soils. More recently, it has been found that phosphate will react also with the silicate clay minerals in soils. The evidence indicates that this latter reaction, because it continues indefinitely, is more complicated than a simple surface reaction, which would reach a definite endpoint with time.

A hypothesis previously suggested by the authors (17) to account for the long-continued reaction of phosphate with kaolinite was based on the assumption that kaolinite is a complex salt of a weak silicic acid and the weak base, aluminum hydroxide. As such, the mineral should dissolve slightly and ionize in solution, and the product of the activities of the dissociating ions should be a constant; that is, the clay should have a solubility-product constant. If the clay dissociates into aluminum cations and silicate anions, it is logical to suppose that phosphate ions will react with the former, disturb the equilibrium, and cause the clay to dissolve. The phosphate would thus be fixed by aluminum in a reaction which might be called "phosphatolysis" by analogy with "hydrolysis."

This hypothesis was tested experimentally by digesting kaolinite in phosphate solutions, analyzing the clay for the phosphorus fixed, and analyzing the solution for the silica released. The results substantiated the hypothesis in that the silica released was proportional to the phosphorus fixed. In addition, extraction of the phosphated clay with aluminum-complexing reagents showed that the aluminum extracted was proportional to the phosphorus extracted, indicating that an aluminum phosphate compound had been formed. The evidence, however, was contradictory to the extent that the ratio of aluminum extracted to phosphorus extracted was not the same as the ratio of silica released to phosphorus fixed. The purpose of the present investigation was to clarify these results.

MATERIALS AND METHODS

Description of kaolinite sample

The kaolinite[2] used throughout the experiments showed a differential thermal curve typical of kaolinite with no evidence of gibbsite. It contained only a trace of iron and exchangeable bases, and its chemical composition closely approximated the theoretical composition for kaolinite. It was not ground in a ball mill but was used with the same particle-size distribution as received (57 per cent finer than 2 μ and 2 per cent finer than 0.2 μ).

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[1] Journal Paper No. J-1748 of the Iowa Agricultural Experiment Station, Ames, Project No. 617. The senior author is now assistant professor of soils, Purdue University.

[2] The kaolinite was "Peerless No. 1 Clay" from Bath, South Carolina. It was furnished through the courtesy of the R. T. Vanderbilt Co., Inc., 230 Park Ave., New York City.

Buffer solutions

A concentrated buffer solution for controlling the pH of the phosphate digestion solutions was prepared by dissolving 123 gm. of sodium acetate in 500 ml. of distilled water and then adding 31.2 ml. of glacial acetic acid. The pH of this solution was 5.35. Hereafter, this buffer solution will be referred to as the "concentrated buffer" solution.

A dilute buffer solution was prepared by diluting 100 ml. of the concentrated buffer to 1 liter. The pH of the solution was 5.1. This solution will be referred to as the "dilute buffer" solution.

Silica determination

Two different dehydration procedures were used in determining silica.

In the first, 60 ml. of 60 per cent perchloric acid was added to 50 to 75 ml. of the solution containing the silica. The resulting solution was evaporated to fumes, boiled gently for 15 minutes, and cooled. Then 125 ml. of distilled water was added, and the solution was immediately filtered, with suction, through Whatman No. 44 paper in Büchner funnels.

In the second procedure, 25 ml. of concentrated sulfuric acid was added to the solution containing the silica, and sufficient distilled water was added to bring the final volume to 100 ml. This solution was evaporated to fumes, cooled to 50 to 70 C., and then mixed with 100 ml. of warm water at about 50°C. The silica precipitate was immediately filtered off through Whatman No. 44 paper in 58° funnels.

In each case the silica determination was completed by ignition in platinum crucibles, weighing, volatilizing the silica residue with hydrofluoric acid, reignition and reweighing. Special precautions (15) were taken to eliminate errors due to the presence of alkali salts in the silica residue.

Phosphorus determination

Phosphorus was determined with an Evelyn photoelectric colorimeter by the method of Dickman and Bray (5). Total phosphorus in the clays was determined in a sodium carbonate fusion. Where phosphorus extraction was studied, phosphorus was determined in the extracts. A check was made on the influence of each extraction reagent on the intensity of color in the colorimetric phosphorus determination. No effect was observed in any case with the dilutions used.

Aluminum determination

Aluminum was determined by a modification of the Lundell and Knowles (18) procedure. Five milliliters of concentrated ammonium hydroxide was added to 100 ml. of the test solution at pH 4.7 to 7.0, containing an excess of 8-hydroxyquinoline. The resulting precipitate was digested at 60° to 70°C. for 10 to 15 minutes after which the solution was cooled and filtered, with suction, through weighed Gooch crucibles. After being washed with cold distilled water, the precipitate was dried at 110°C. and weighed. Tests showed the presence of aluminum-complexing reagents in the solution to have no effect on the precipitation of aluminum by 8-hydroxyquinoline when this procedure was used.

Washing of phosphated kaolinite

At the conclusion of the phosphate-fixation period the clay suspension was centrifuged and the phosphate solution was poured off. To remove excess phosphate, the clay was then washed four to six times in the centrifuge, 50-ml. portions of the dilute buffer solution being used. Tests of the washing solution showed that this procedure removed the excess phosphate.

RESULTS

Phosphorus fixation and silica release

As a test of the hypothesis that kaolinite has a solubility-product constant and is decomposed by phosphate, the amounts of silica released and phosphate fixed upon treatment of kaolinite with phosphate were determined. Samples of 1 gm. and 0.5 gm. of kaolinite in stoppered, 100-ml. Lusteroid[3] centrifuge tubes were heated at 45°C. for 2 weeks and 3 weeks, respectively, with 75 ml. of water containing potassium dihydrogen phosphate in concentrations ranging from 0 to 3 *N*. In each case the reaction was adjusted to pH 4.8 to 5.1 by inclusion of 5 ml. of the concentrated buffer solution. At the end of the reaction period the clays were centrifuged out and a 50-ml. aliquot of the supernatant liquid was analyzed for silica by the sulfuric acid dehydration procedure. The clay samples were washed as described previously. Total phosphorus was determined in the 1-gm. samples by the sodium carbonate fusion method. The 0.5-gm. samples were extracted with 60 ml. of 0.5 *M* ammonium malonate (pH 4.6) for 5 days. Aliquots of the extract were then analyzed for phosphorus and aluminum.

Figure 1 shows that there was a relationship between the amount of phosphorus fixed and the amount of silica released. Since the kaolinite used in these experiments contained no free silica, as evidenced by a free silica determination (26, p. 518), the silica in solution must have come from the clay.

The break in the curve at approximately 20 millimoles of phosphorus fixed indicates that at least two different reactions occurred. If the two reactions had occurred simultaneously, only one line would have been obtained. It appears, therefore, that about 20 millimoles of phosphorus was fixed by a reaction in which molar ratio of phosphorus fixed to silica released was 0.89:1 before the second reaction began. From these data no conclusion can be drawn as to whether the first reaction terminated as the second reaction began.

Products of phosphorus fixation

According to the solubility-product hypothesis, the phosphatolysis of kaolinite should result in precipitation of an aluminum phosphate compound. To detect the possible presence of such a compound, use was made of certain organic reagents which differed in their tendency to form soluble chelate complexes with aluminum.

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[3] Lusteroid is a trade name for a material resembling cellulose acetate. The purpose of using these tubes was to eliminate the possibility of silica contamination from the container during the experiment.

Theoretically, the essential conditions for formation of chelate rings are that the organic radical must contain acidic or coordinating groups or a combination of these functional groups separated by chains of suitable length for production of five- or six-membered rings with the metal ion. Only such rings are stable because of the strain introduced in larger or smaller rings by the changing of the natural bond angles. The metal ion may be implicated in one or more of these rings depending upon its primary and secondary valences. Diehl (7), Ephraim (9), and others have discussed the formation and characteristics of chelate rings and coordination compounds.

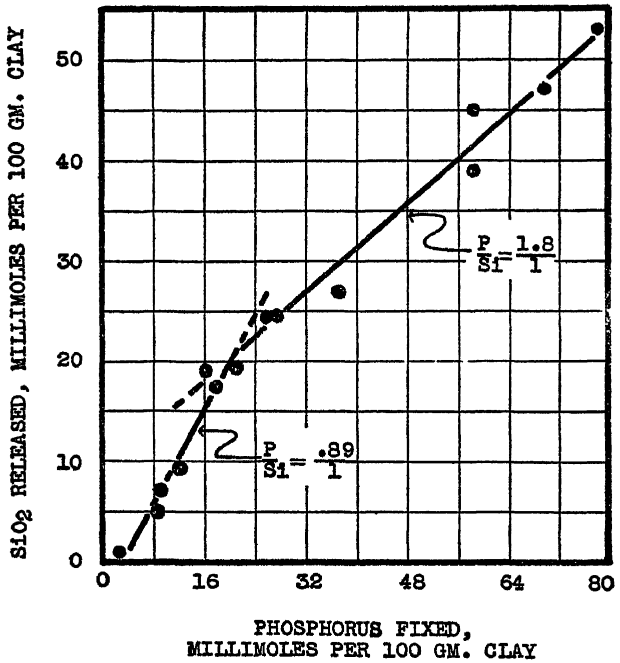

Fig. 1. Molar Relationship Between Silica Released and Phosphorus Fixed by Kaolinite

In the experiment a phosphated kaolinite was prepared by treating 20 gm. of kaolinite for 2 weeks at 45°C. with a 4.5 *N* phosphate solution adjusted to pH 4.2. Washing was carried out as with other samples. Samples of 0.5 gm. of this phosphated kaolinite were extracted for 24 hours at 45°C. with 60-ml. portions of various reagents. Each reagent except oxalate was used at a concentration of 0.5 M, and the reaction was adjusted to pH 7 with ammonium hydroxide. Oxalate was used in a saturated solution at pH 7. At the end of the reaction period, aliquots of the solutions were analyzed for phosphorus. Parallel determinations were made on 100-mgm. samples of c.p. aluminum phosphate using a 48-hour extraction period. The results are shown in figure 2.

Two facts are obvious: first, there was a correlation between the phosphorus extracted from the clay and that extracted from the aluminum phosphate, and second, considerably more phosphorus was extracted by the aluminum-complexing reagents than by the noncomplexing reagents. These results indicate that the fixed phosphorus was combined with aluminum.

It is especially instructive to compare the extracting power of complex-forming reagents with that of non-complex-forming reagents of the same class or of the same homologous series; for example, oxalic acid [$(COOH)_2$] and malonic acid [$CH_2(COOH)_2$] differ from succinic acid ($HOOCCH_2CH_2COOH$) only by two and one CH_2 groups, respectively, but the first two acids extracted considerably more phosphorus than the latter. The behavior is apparently related to the size and stability of the rings formed by these acids with aluminum. Oxalic acid and malonic acid form stable five- and six-membered rings, respectively, whereas succinic acid would form an unstable seven-membered ring.

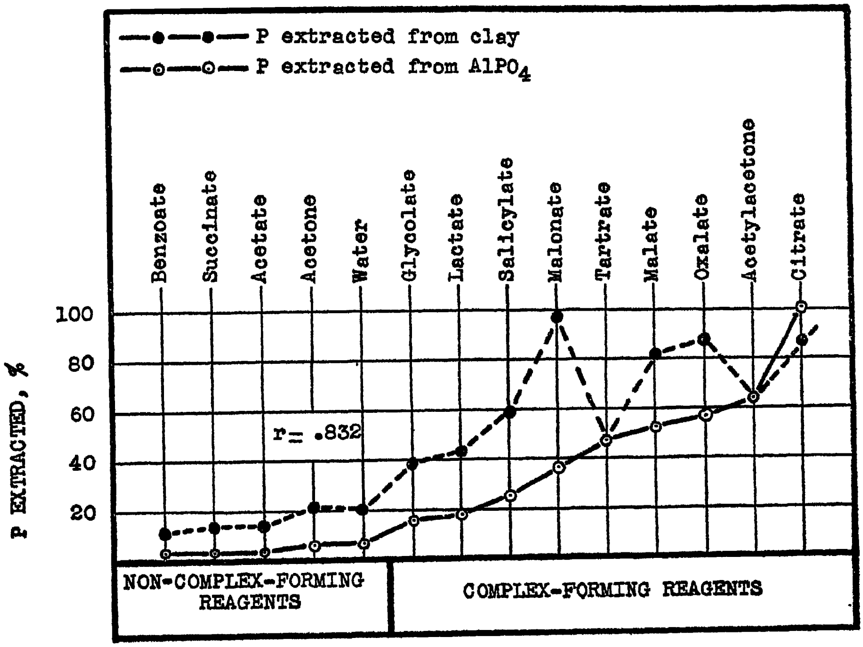

FIG. 2. EXTRACTION OF PHOSPHORUS FROM ALUMINUM PHOSPHATE AND FROM PHOSPHATED KAOLINITE BY VARIOUS COMPLEX-FORMING AND NON-COMPLEX-FORMING REAGENTS

Salicylic (o-HOC_6H_4COOH) and benzoic (C_6H_5COOH) acids differ by only a hydroxyl group, and yet the former extracted much more phosphorus than the latter. The hydroxyl group in the ortho position on the salicylic acid permits the formation of a six-membered ring with aluminum.

Acetylacetone ($CH_3COCH_2COCH_3$) and acetone (CH_3COCH_3) differ in that the former is a diketone and the latter a ketone. Acetylacetone extracted much more phosphorus than did acetone. Enolization of the acetylacetone permits the formation of a six-membered ring with aluminum.

The reagents acetylacetone, tartrate, and malonate occupy different positions in the two extraction sequences. The reason for this is not known. A strict comparison of the extraction sequences can be made only when equilibrium has been reached between the phosphate compounds and the extracting reagents. Better agreement might be obtained at equilibrium. Another factor to be considered is the possibility that in the warm solutions the surface reactivity of the clay might catalyze such side reactions as decarboxylation of the organic acids.

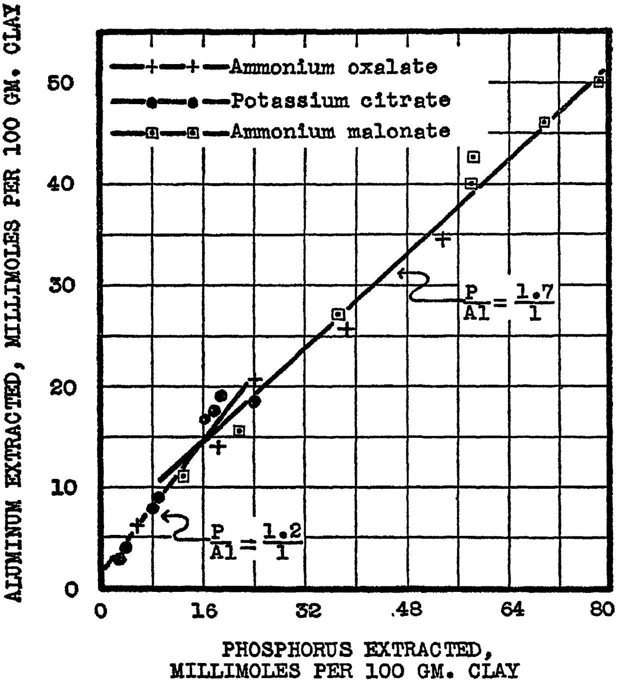

FIG. 3. MOLAR RELATIONSHIP BETWEEN ALUMINUM AND PHOSPHORUS EXTRACTED FROM PHOSPHATED KAOLINITE BY COMPLEX-FORMING REAGENTS

Extraction of the products of phosphorus fixation

The data presented in the preceding section indicate that the phosphorus in the phosphated clay was combined with aluminum. To obtain further evidence on the nature of the phosphate in phosphated kaolinite, an experiment was conducted in which analyses were made for both phosphorus and aluminum in the extracts. One-gram samples of clay in 100-ml. centrifuge tubes were phosphated at 45°C. for 2 weeks with 75 ml. of a water solution of potassium dihydrogen phosphate in phosphate concentrations ranging from 0 to 3.5 *N*. In addition to the phosphate, each solution contained 5 ml. of concentrated buffer solution to adjust the reaction to pH 4.8 to 5.1. At the conclusion of the reaction period the clays were washed thoroughly, as described earlier, and then 60 ml. of extracting reagent was added and allowed to react with the clay at 45°C. for 2 days. Aliquots of the extraction reagents were then removed and analyzed for phosphorus and aluminum. The extraction reagents used in these experiments were potassium citrate and ammonium oxalate. The results, shown graphically in figure 3, include also the ammonium malonate extraction data from the decomposition experiment described earlier.

It is evident that the relationship between the phosphorus and aluminum extracted may be represented by two straight lines intersecting at approximately 17 millimoles of phosphorus extracted. The molar P:Al ratio was 1.2:1 below 17 millimoles of phosphorus extracted and 1.7:1 above 17 millimoles. From these ratios it appears that two different aluminum phosphate compounds were formed.

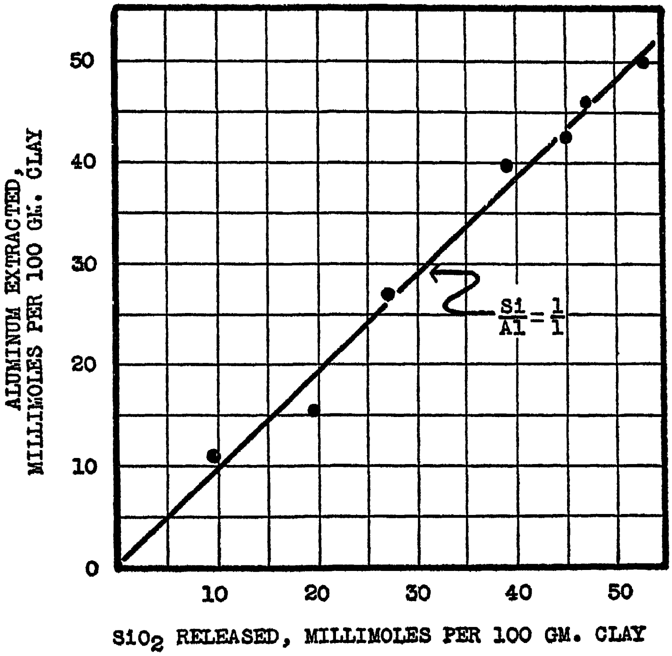

FIG. 4. MOLAR RELATIONSHIP BETWEEN SILICA RELEASED AND EXTRACTABLE ALUMINUM PRODUCED DURING PHOSPHORUS FIXATION

In kaolinite the molar Si:Al ratio is 1:1. Each time an atom of silicon is involved in reaction with phosphate, an atom of aluminum should likewise be involved. For this reason it would be expected that for each mole of silica released during phosphate fixation it should be possible subsequently to extract a mole of aluminum from the phosphated clay. The results obtained in the second reaction (above 17 millimoles of P extracted) were in agreement with this line of reasoning, the molar Si:Al ratio being 0.95:1. The data obtained in the decomposition experiment were likewise in agreement, the molar Si:Al ratio being 1.05:1 (fig. 4). In the first reaction (less than 17 millimoles of P extracted), however, the ratio was 1.35:1, calculated on the basis of the phosphorus involved in each case. This variation from a ratio of unity in the first reaction may have real significance.

On the other hand, it may be merely a matter of experimental error in dealing with the smaller amounts of constituents. As the data on the P:Si and P:Al ratios for the first reaction were obtained on different sets of samples, it was not posible to determine the Si:Al:P ratios for a given sample. Moreover, the excess of silica over phosphorus in the first reaction is difficult to account for in any way other than low values for phosphorus, in view of the evidence from figure 5 that easily replaceable silica was absent. Until more definite evidence is available to show that the Si:Al ratio in the first reaction is different from that in the second, it will be assumed that the ratio was in all cases unity.

In an earlier experiment (17) only one P:Si ratio and one P:Al ratio were obtained. These ratios were not the same. In the present investigation two P:Si and two P:Al ratios were obtained and the P:Si ratios were essentially the same as the P:Al ratios. As yet, the discrepancies between the two experiments have not been satisfactorily explained. It is possible, however, that the higher temperature (60°C.) of the earlier experiment precluded formation of the product of the first reaction because, as will be shown later, this product is relatively unstable.

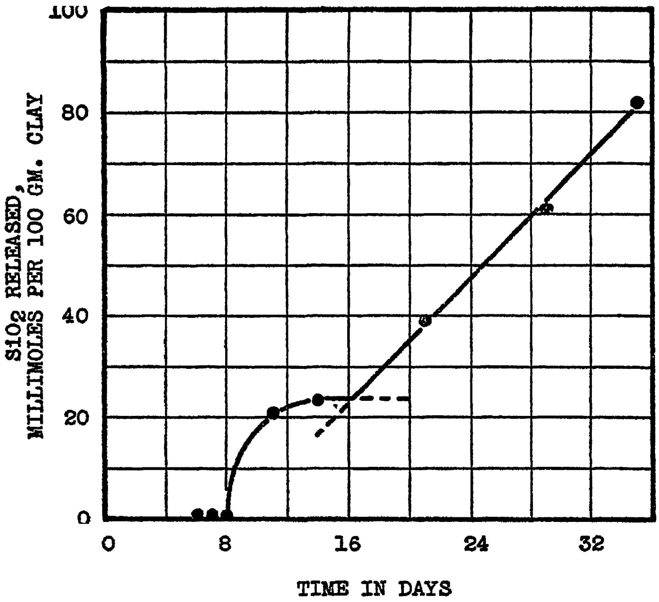

FIG. 5. RATE OF SILICA RELEASE FROM KAOLINITE IN PRESENCE OF PHOSPHATE

Time-rate of silica release

The findings described thus far indicate that two different reactions occurred to produce two different compounds in the fixation process. To obtain further information as to the nature of the reactions, an experiment was designed to determine the rate of silica release.

In this experiment 0.5-gm. samples of clay in Lusteroid centrifuge tubes were digested for different intervals in a water bath at 45°C. with 75-ml. portions of a potassium dihydrogen phosphate solution 3 *N* to phosphate and buffered at pH 4.8 with 5 ml. of the concentrated buffer. As each tube was removed, the clay was centrifuged out and an aliquot of the solution was analyzed for silica by the sulfuric acid dehydration procedure. As preliminary experiments had shown that no phosphorus was fixed for at least 6 days, no analyses were made until the sixth day. All samples were run in triplicate except for those removed between 6 and 11 days, in which only single samples were run. The data are presented in figure 5.

At least two different reactions evidently occurred in the fixation process. The first was a typical adsorption type with a surface saturation corresponding to 24 millimoles of silica released. The release of 24 millimoles of silica means the fixation of a similar amount of phosphate, since data in the preceding section indicated that approximately equivalent quantities of phosphorus, silica, and aluminum were involved in the first reaction. Thus, as phosphate was fixed, silica was released and aluminum was changed to a form extractable, along with the phosphate, by aluminum-complexing reagents. It is reasonable to postulate, therefore, that an isomorphous exchange of phosphorus tetrahedra for silicon tetrahedra occurred on the surface of the clay. This type of replacement should occur largely on crystal edges and corners. The possibility of such a substitution has been suggested before (2, 19), and Mattson and Hester (20) and Toth (29) have found that phosphate fixation by soil colloids results in the release of silica.

No satisfactory explanation can be given for the 8-day induction period preceding the start of the reaction. Undoubtedly a small amount of phosphorus reacted with the clay during this period, as will be shown later, but it was probably removed by the dilute buffer solution used in washing the clay. Temperature appears to be a factor in the induction period, since preliminary experiments showed that considerable silica was released from the clay in 48 hours at the higher temperature of 60°C.

The rate of the second reaction was a linear function of time. This reaction did not begin until the first reaction was completed, as evidenced by the horizontal part of the first curve. Apparently, the second reaction was dependent on the first. An explanation for this behavior may be made on the basis of consecutive reactions.

If the interpretation of the data is correct, the first reaction represents the isomorphous replacement of surface silicon tetrahedra by phosphorus tetrahedra. This replacement would probably result in an unstable phosphate compound because there is an infraction of the electrostatic valence rule when two phosphorus tetrahedra share a common oxygen ion (23). It is probable, therefore, that the surface compound would decompose in favor of a more stable precipitated phosphate. Consequently, the second reaction could represent the phosphate-induced decomposition of the surface compound and the subsequent precipitation of an aluminum phosphate of higher phosphorus content.

Thus, the aluminum phosphate on the surface might dissolve, react with more phosphate, and precipitate. As fresh surface became exposed, it should again react with phosphate in solution. Since the rate of adsorption prior to surface saturation appeared to be greater than the rate of solution, the surface phosphate could be maintained near the saturation value as long as the concentration of phosphate in solution remained high. Why the solution and secondary precipitation did not start as saturation of the surface was approached is problematical. Perhaps the formation of aluminum phosphate nuclei for precipitation on the inactive surface of the clay was the limiting factor in the initiation of this reaction.

Corroborative evidence for the proposal that the second reaction was a solution reaction may be obtained by consideration of equations which represent the solution of crystals (21; 24, p. 284). These equations may be expressed as follows:

$$-\frac{dc}{dt} = kSc$$

$$-\frac{dc}{dt} = kS\frac{dc}{dn}$$

where c is the concentration of the reagent or solvent effecting the solution (phosphate ions in this case), t is the time, k is a constant, S is the active surface area, and n is the distance normal to the surface. The first equation is applicable when the reaction at the interface is slow compared with diffusion, and the second equation is applicable when the rate of diffusion is slow compared with the rate of the reaction at the interface.

It has been pointed out that the dissolving surface should be maintained essentially constant as long as the phosphate concentration in solution remains high. In this experiment the phosphate concentrations were sufficiently high that little change in concentration ocurred during the limited period of the reaction. The values c, S and $\frac{dc}{dn}$ in the preceding equations should, therefore, be essentially constant, and the rate of solution should be a linear function of time. The experimental data are in agreement with this prediction.

From the evidence submitted in this section, it appears that the phosphatolysis of kaolinite is accomplished by two consecutive reactions. Indications are that the first reaction is a surface reaction in which phosphorus tetrahedra replace silicon tetrahedra to produce an unstable surface compound, and the second reaction is the phosphate-induced solution of this surface compound and the precipitation of an aluminum phosphate compound.

Time-rate of phosphorus and aluminum extraction

The extraction of phosphorus from the clay, whether it be from the surface or from a precipitate, should obey one of the equations presented in the previous section, because the phosphorus is extracted by dissolving the compound in which it is combined. From these equations it is obvious that if the concentration of the extracting reagent is sufficiently great to remain essentially constant during the extraction, the only variable affecting the reaction rate will be the area of the active surface. The following experiment was designed to investigate the active surface of the phosphate compounds.

One-gram samples of phosphated kaolinite[4] were digested in 100-ml. centrifuge tubes at 45°C. with 60-ml. portions of a 0.5 *M* potassium citrate solution at pH 4.7 for periods up to 13 days. One tube was removed from the water bath each day, the clay was centrifuged out, and aliquots of the supernatant liquid were taken for phosphorus and aluminum determinations. The data are presented in figure 6. Only the data up to 5 days' extraction are plotted because 96 per cent of the phosphorus extractable by the citrate had been removed by the fifth day and beyond this time the data became somewhat erratic.

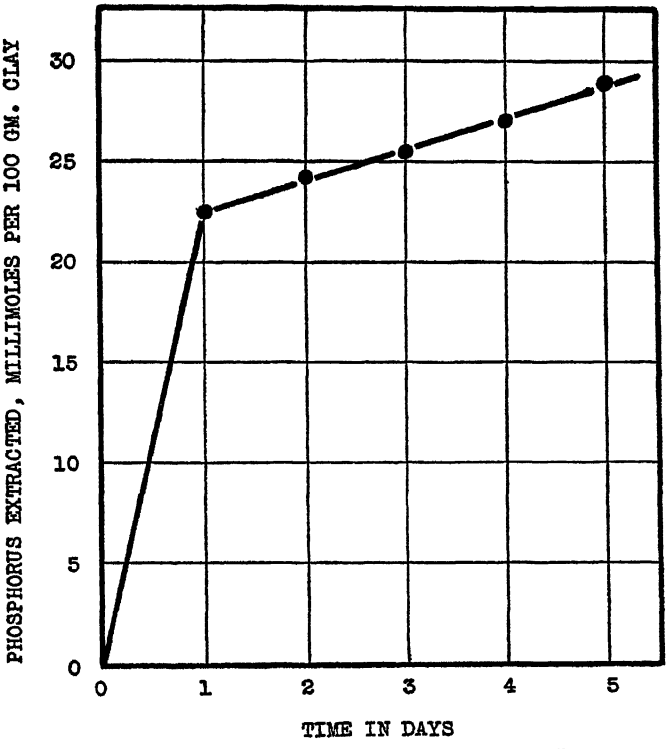

FIG. 6. RATE OF EXTRACTION OF PHOSPHORUS FROM PHOSPHATED KAOLINITE BY POTASSIUM CITRATE

Obviously, the phosphorus was extracted at different rates, the faster rate obtaining for the first 23 millimoles, all extracted in one day. It should be recalled that the P:Si ratio changed at about 20 millimoles, the P:Al ratio changed at about 17 millimoles, and the surface reaction had a saturation value of about 24 millimoles of phosphorus per 100 gm. of clay. It is therefore consistent with the data to conclude that 17 to 24 millimoles of phosphorus per 100 gm. of clay was fixed by a surface reaction in which phosphorus tetrahedra replaced silicon tetrahedra and that this phosphate was more readily dissolved than was the phosphate fixed in excess of 17 to 24 millimoles per 100 gm. of clay.

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[4] This clay was the same as that used in the experiment on phosphorus extraction by the various complex-forming and non-complex-forming reagents.

The phosphorus in excess of 23 millimoles per 100 gm. of clay was extracted with more difficulty, and the rate of extraction was a linear function of time. According to the equations and discussion in the preceding section, it may be concluded from the linear extraction rate that the surface area remained essentially constant during the extraction. Since the fixation process in this case was presumably the dissolution of the surface layer and a secondary precipitation of the phosphate, a reasonable explanation for the constant surface area throughout the extraction process is that as the aluminum phosphate was formed, it diffused from the actively dissolving surface and precipitated as a thin film on a more inert part of the clay surface. The film would provide a constant dissolving surface during extraction.

TABLE 1

Extraction of aluminum and phosphorus from kaolinite by ammonium oxalate and ammonium malonate

EXTRACTING REAGENT	EXTRACTION PERIOD	P EXTRACTED PER 100 GM. CLAY*	Al EXTRACTED PER 100 GM. CLAY	P:Al MOLAR RATIO
	days	*mmol.*	*mmol.*	
Ammonium oxalate	5	35.3	28.6	1.23:1
	9	29.7	30.4	0.98:1
	16	37.1	33.8	1.10:1
Ammonium malonate	5	36.8	27.3	1.35:1
	9	35.2	27.5	1.28:1
	16	36.8	30.4	1.21:1

* The total phosphorus content of the clay was 36.3 millimoles per 100 gm. as determined by sodium carbonate fusion.

Since it was desirable to know whether all the phosphorus could be extracted with a complex-forming reagent, 1-gm. samples of the phosphated clay used in the citrate experiment were extracted at pH 4.7 with 60-ml. portions of saturated ammonium oxalate and 0.5 *M* ammonium malonate. At the end of the 5-, 9-, and 16-day extraction periods, aliquots of the extraction solution were analyzed for phosphorus and aluminum. The results are shown in table 1.

After 5 days, both the oxalate and the malonate had extracted all the phosphate within the limits of experimental error. As in the citrate extraction, the aluminum extracted was proportional to the phosphorus extracted throughout the entire experimental period.

Adsorption of phosphorus from dilute solutions

The adsorption equation. The fixation experiments in the preceding sections were all conducted with concentrated phosphate solutions. Since so much experimental work on phosphorus fixation has been done in dilute solutions, the possibility of a dilute-solution reaction over short periods was investigated.

Ten-gram samples of kaolinite in 100-ml. centrifuge tubes were shaken at room temperature for 1½ hours with 50 ml. of dilute potassium dihydrogen phosphate solution ranging in concentration from 0.005 to 0.05 mgm. of phosphorus per milliliter. The pH of the original solution was 5.0. At the end of the reaction period the clay was centrifuged out, and the content of phosphorus in the supernatant liquid was determined. The results are recorded in figure 7.

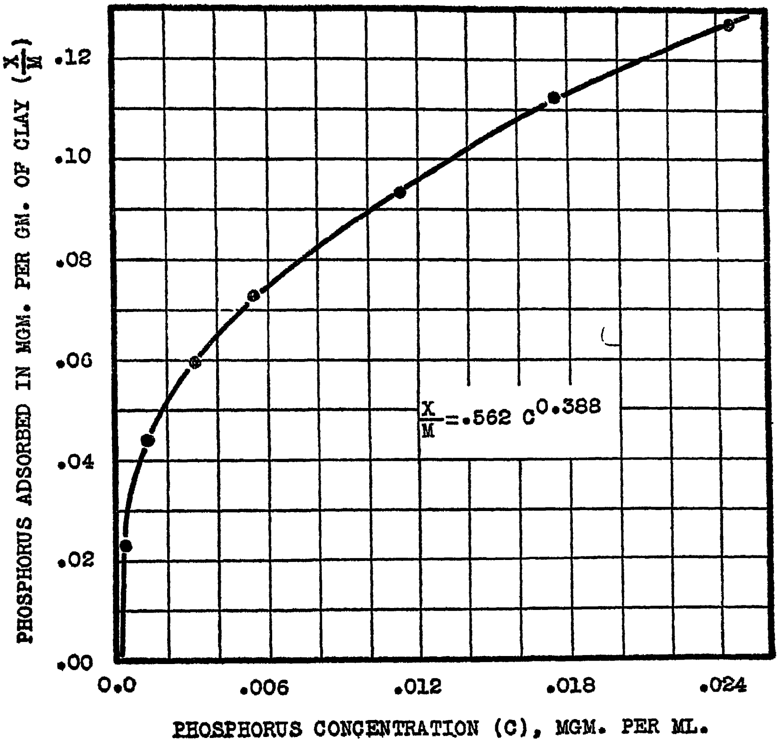

FIG. 7. ADSORPTION OF PHOSPHATE FROM DILUTE SOLUTIONS BY KAOLINITE

The plot of the amount of phosphorus fixed against the final concentration in the solution produced a typical adsorption curve, which could be represented by the Freundlich adsorption equation

$$\frac{x}{m} = kc^{1/n}$$

where x is the amount of the solute adsorbed, m is the weight of the adsorbent, k is a proportionality constant, c is the concentration of the solute in the equilibrium solution, and n is a constant. Obedience to this equation is an indication that adsorption equilibrium had been reached within the relatively short period of 1½ hours.

From the work of Kolthoff (13), who showed theoretically that the Freundlich equation can represent exchange reactions when applied to ions, it might be postulated that the adsorption was an exchange reaction. However, since the curve began to level off when as little as 0.13 mgm. of phosphorus per gram of clay (0.42 millimole per 100 gm. of clay) had been adsorbed, it appears that this adsorption and the adsorption that displaced the silica (saturation at 24 millimoles per 100 gm. of clay) are not the same. It is plausible to assume, therefore, that if an exchange occurred it was between phosphate and hydroxyl ions.✓

✓*Effect of temperature on adsorption.* Two different types of adsorption may occur; namely, chemical reaction with the surface, and physical adsorption. The former type is distinguished from the latter by the larger energy of adsorption and by the shorter range of the forces involved. In either type, however, an equilibrium occurs between adsorbed molecules and the molecules in solution. This equilibrium is dependent on temperature, as expressed by the integrated form of the van't Hoff equation,

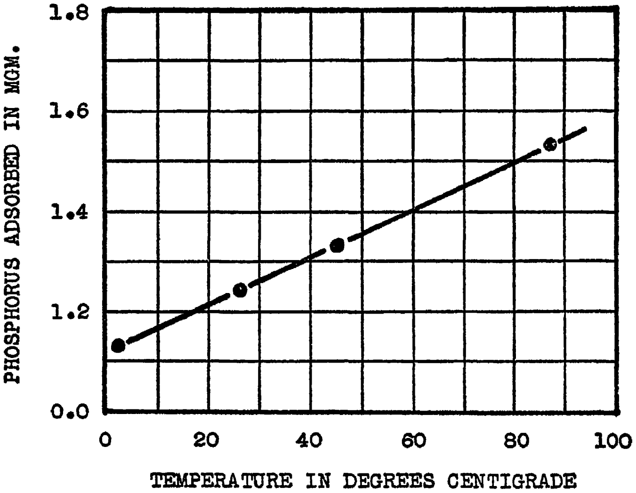

FIG. 8. ADSORPTION OF PHOSPHATE BY KAOLINITE AT DIFFERENT TEMPERATURES

$$\mathit{ln}\ K = -\frac{\Delta H^\circ}{RT} + \text{constant},$$

where K is the equilibrium constant, R is the molar gas constant, T is the temperature and ΔH° is the heat of reaction when the reactants and products are in their standard states.

It is seen that if ΔH° is negative (heat is evolved in the reaction), an increase in temperature will decrease the amounts of the products formed, whereas if ΔH° is positive (heat is absorbed in the reaction), an increase in temperature will increase the amounts of the products formed. Physical adsorption always has a negative heat of adsorption, but chemical adsorption may have either a positive or negative heat of adsorption.

To investigate the effect of temperature on the adsorption of phosphate from dilute solution, 10-gm. samples of kaolinite in 100-ml. centrifuge tubes were shaken periodically for 3 hours at different temperatures with 50-ml. portions of a solution containing 0.05 mgm. of phosphorus as potassium dihydrogen phosphate per milliliter of solution. The clay was then centrifuged out and the supernatant liquid was analyzed for phosphorus. The results in figure 8 show clearly that there was increasing adsorption of phosphate with increasing temperature. Therefore, if the temperature factor did not change the nature of the reaction the standard heat of reaction was positive and the adsorption was chemical.

Since the exchange of phosphate ions for the hydroxyl ions of a crystal lattice is a type of chemical adsorption, these experiments lend weight to the hydroxyl replacement theory. No decision can be made, however, as to whether the seat of the exchange is the clay or sesquioxide impurities. A minute quantity of hydrated sesquioxides would be sufficient to account for the observed results.

DISCUSSION

The investigation described in this paper was undertaken to examine the validity of the hypothesis that phosphate will decompose kaolinite by disturbing the equilibrium between the clay and its component ions in solution. The experimental data substantiate the hypothesis, since, upon fixation of phosphate by kaolinite, silica is released and aluminum is changed to a form extractable with aluminum-complexing reagents. In the course of the investigation, however, it became evident that more than one reaction was occurring. The phosphatolysis of kaolinite is apparently accomplished by two consecutive reactions, the isomorphous replacement of silicon tetrahedra by phosphorus tetrahedra and the phosphate-induced decomposition of this adsorbed layer. In addition, there is evidence for the surface exchange of phosphate ions for hydroxyl ions.

The soil system differs from the laboratory system in the variables temperature, phosphate concentration, and composition of the substrate. The question naturally arises, therefore, whether these reactions will occur in the soil. The following considerations are pertinent to this problem.

Variations in temperature change only the magnitude of the equilibrium constant and the rate of the reaction but do not determine whether the reaction can occur. Consequently, a reaction taking place at one temperature should take place at another temperature provided other conditions are satisfactory. The difference between the experimental temperature and the normal surface temperature of the soil in summer was about 15° to 20°C. It seems reasonable to conclude, therefore, that the difference in temperature between the laboratory and soil systems does not preclude the field occurrence of the reactions observed in the laboratory.

In view of the instability of the silicate-exchangeable phosphate and the low phosphate concentration of the soil solution, it is doubtful that this type of fixed phosphorus occurs to any extent in the soil. Even a limited amount of silicate exchange might, however, be a significant factor in phosphorus fixation with the relatively small amounts of phosphate fertilizers added under field conditions.

Evidence for phosphatolysis of the clay in the soil is furnished by the continued fixation of phosphorus with time (14)[5]. Similar evidence has been obtained with clay minerals in phosphate solutions which were comparable in strength to the soil solution (1, 4, 6, 22, 25). Black (1) found that in phosphate solutions containing 1, 10, and 100 ppm. of phosphorus a much greater amount of phosphorus was fixed by kaolinite in 1 month than in 48 hours. Over the 48-hour period there was a maximum fixation at pH 6 to 7. As the concentration was increased through 10 to 100 ppm., a second maximum at about pH 3 became noticeable. At each concentration the maximum at pH 3 became more noticeable with time. Since the maximum precipitation of aluminum phosphate is between pH 3 and 4 (3, 10, 27), it may be inferred that increasing the phosphate concentration of the solution or increasing the time of reaction caused increasing phosphatolysis of the clay with precipitation of aluminum phosphate. The maximum at pH 6 to 7 changed relatively little in magnitude with time. It is reasonable to suppose, therefore, that this reaction represented true adsorption. The lowest concentration of phosphate used in Black's experiment is not dissimilar to the concentration in the soil solution.

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[5] Steele, J. G. The effect of other anions on the retention of phosphate by colloidal clays. 1934. [Unpublished Ph.D. thesis. Copy on file Ohio State University, Columbus.]

The hydrolysis of clays is generally considered to be a common weathering process. If hydrolysis of clays occurs in a solution containing hydrogen and hydroxyl ions in concentrations of 10^{-7} N, it is plausible that phosphate ions at a concentration of 10^{-4} N (about 1 ppm.) will cause phosphatolysis of the clay. There is considerable evidence in the geological literature (11, 12, 16, 28) that over long periods of time aluminous minerals may be altered to aluminum phosphate under the influence of percolating waters containing phosphate derived from guano beds. Ensminger (8) recently found that the x-ray patterns produced in kaolinite and Cecil soil colloid upon treatment with phosphate were similar to those produced when aluminum oxide and hydrous aluminum oxide were treated with phosphate.

As was pointed out earlier, the pure kaolinite used in the laboratory experiments is not entirely analogous to soils. In many soils, however, kaolinite is a major constituent of the clay fraction. The fixation of phosphate by kaolinite is a distinct possibility in these soils. In nonkaolinitic soils other clay minerals predominate in the clay fraction. It is likely that the reactions of phosphate with these minerals are analogous to the reactions that occur with kaolinite. In consequence, the reactions discussed in this paper are probably of widespread occurrence in soils.

SUMMARY

The hypothesis was presented that kaolinite dissociates into aluminum and silicate ions and that phosphate precipitates the aluminum ions, thereby disturbing the equilibrium and causing the clay to dissolve in accordance with solubility-product principles. As would be predicted from the hypothesis, the digestion of kaolinite in phosphate solutions resulted in a release of silica which was proportional to the phosphorus fixed. The slopes of the silica-released:phosphorus-fixed lines indicate that two different reactions occurred in the fixation of phosphorus.

Extraction of phosphated kaolinite with various reagents showed that alumi-

num-complexing reagents extracted more phosphorus than did non-complex-forming reagents and that the extraction of aluminum was proportional to the extraction of phosphorus. The slopes of the aluminum-extracted:phosphorus-extracted lines were essentially the same as the slopes of the silica-released:phosphorus-fixed lines. The conclusion was drawn from these results that two different aluminum phosphate compounds had been produced in the clay.

The rate of release of silica during phosphorus fixation by kaolinite varied with time, indicating the existence of two different reactions, the first and more rapid of which was completed before the second reaction began. The first reaction was apparently the surface replacement of silicon tetrahedra by phosphorus tetrahedra, and the second was apparently the phosphate-induced decomposition of the surface phosphate with subsequent precipitation of an aluminum phosphate compound.

Phosphorus extraction by aluminum-complexing reagents was found to occur at two different rates. The amount of phosphorus extracted at the more rapid rate corresponded with that involved in the first reaction described above.

Fixation of phosphate by kaolinite from dilute solution obeyed the Freundlich adsorption isotherm and increased with temperature, the latter being a criterion of chemical adsorption. Since the amount of phosphate involved in this reaction was small compared with that involved in the silica release, it was concluded that the dilute-solution adsorption represented a different reaction—perhaps the replacement of surface hydroxyl groups by phosphate groups.

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USE OF VOLATILE SILICONES TO INCREASE WATER-STABILITY OF SOIL

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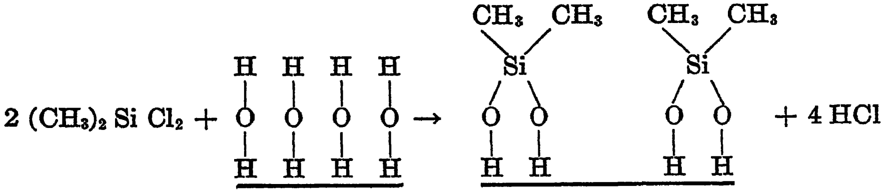
Received for publication January 30, 1950

Soil aggregates can be dispersed either under natural conditions or in the laboratory by slaking in water and by a subsequent impact of running or falling water. In the field the result may be an undesirable sealing of the soil surface. In addition, the destruction of the aggregates is the necessary preconditioning of soil for erosion, and the stability of soil aggregates against the destructive action of water is highly correlated with degree of erosion (6). These facts are the basis for the wet-sieving technique to evaluate soil structure (9). In using this method the soil should be prewetted gradually to avoid compression of air inside the aggregates (4), because sudden wetting is very destructive to aggregates.

If the speed of water imbibition could be further lowered by decreasing the wettability of the soil, it might possibly be found that its water-stability had increased. McCalla (2) reported that addition of waxy and resinous materials increased markedly the water-stability of soil.

Soil used for construction purposes also should be "water-stable," although the term is used in a different sense, since soil engineers are interested in treatments that render earth structures less likely to fail under wet conditions. It has been found by Winterkorn *et al.* (8) and by Davidson[2] that waterproofing compounds such as resinous materials and high-molecular amino-cations are effective in improving the engineering properties of soil as indicated directly by bearing tests or indirectly by determining the plastic index (1).

The recent development of silicone chemistry has yielded some excellent waterproofing agents, some of which are unique in that they may be applied as vapors under ordinary temperatures and pressures. Two of these are methyltrichlorosilane and dimethyldichlorosilane, which hydrolyze with a water film present on an object and form a polymerized organo-silicon layer that is very water-repellent. In the course of the reaction, hydrochloric acid is liberated. The reaction for dimethyldichlorosilane has been schematically presented by Norton (3) as follows:



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[1] Journal Paper No. J-1741, Iowa Agricultural Experiment Station, Project 739. The author is now research assistant professor, North Carolina Agricultural Experiment Station.

[2] Davidson, D. Effect of large organic cations on physico-colloidal properties related to

In view of the preceding paragraphs, it was thought that a moderate treatment of air-dry soil with methylchlorosilanes might improve the water-stability as measured by wet-sieving and by soil engineering standards. The present paper describes experiments to evaluate this effect.

MATERIALS AND METHODS

A commercially available mixture[3] of 2 parts by weight of dimethyldichlorosilane and 1 part by weight methyltrichlorosilane was used. This is a clear liquid with a boiling point of approximately 70°C., sp. gr. 1.125, toxic, flammable, and corrosive. One gram of this mixture—henceforth designated "MCS"—will react with 0.332 gm. of water.

The treatment was effected by placing a maximum of 80 gm. of air-dry soil in a Petri dish and evacuating with an aspirator pump in a vacuum desiccator. The desiccator was fitted with an inlet with glass stopcock. After the desiccator was evacuated, the desired amount of MCS was transferred into the inlet and driven into the desiccator by opening the stopcock carefully. The liquid evaporated instantaneously and penetrated the soil. After 5 to 10 minutes, air was let in and the soil was taken out and aired for a minimum of 30 minutes to eliminate HCl vapors.

To determine the distribution of water-stable aggregates, the Yoder technique of wet-sieving (9) was used on 25-gm. air-dry samples with sieving time of 30 minutes. The samples were wetted by spraying with a fine mist, and 5 minutes was allowed for imbibition of the water. The mean weight-diameter of the water-stable aggregates was calculated from the data by a method proposed by Van Bavel (5). The plastic index was determined according to official methods (1).

The soils used for aggregate analysis were passed through a screen, with 8-mm. openings, in the field and were air-dried in the laboratory. The soils used for determining the plastic index were air-dried and passed through a 40-mesh screen, according to the official procedure. Aggregate analyses were made on Marshall silt loam, Ida silt loam, and Clarion loam. Plastic indexes were determined on Marshall silt loam, Ida silt loam, Mankato till, and Edina subsoil (plastic till).[4]

The air-dry soils contained 3 to 4 per cent water. Treatment was effected at rates of 0.2 and 0.5 per cent MCS by weight on the basis of the air-dry soil. Obviously, then, only a fraction of the water present in the soil, namely, between 2 and 5 per cent, entered the reaction.

EXPERIMENTAL RESULTS

Table 1 shows the effect on aggregation of treatment of Marshall silt loam from a continuous corn plot, which was sampled in July 1949. For comparison,

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soil stability. 1948. [Unpublished doctoral thesis. Copy on file Iowa State College Library, Ames.]

[3] Sold under the trade name DC 1208 by Dow Corning Corp., Midland, Michigan.

[4] Descriptions of the soils used may be found in "Principal upland soils of Iowa" Iowa Agr. Exp. Sta. Agron. 49 (Rev.) [Mimeographed].

season averages of aggregate determinations on Marshall silt loam in corn of a corn-oats-meadow rotation made 2 years earlier by Gish[5] are also shown.

It appears from table 1 that the effect of treatment is considerable and that the differences obtained are of an order of magnitude comparable with the difference between the soil of a plot that had been in continuous corn for 15 years and the soil of a plot next to it that had been for the same length of time in a rotation considered satisfactory for reducing erosion on a 9 per cent slope. A larger effect was found on Ida silt loam—treated at one rate only (table 2)—and on

TABLE 1

Effect of MCS treatments on aggregate distribution and mean weight-diameter of Marshall silt loam from a continuous corn plot, in comparison with untreated soil from a corn plot in corn-oats-meadow rotation

AGGREGATE SIZE	AGGREGATE DISTRIBUTION			
	Continuous corn plot			Rotation corn plot
	Untreated	0.2 per cent MCS	0.5 per cent MCS	Untreated
mm.	*per cent**	*per cent**	*per cent**	*per cent**
8.0 -2.0	4.1	8.8	9.7	14.3
2.0 -1.0	10.7	11.5	15.8	9.1
1.0 -0.5	11.8	14.2	17.5	12.8
0.5 -0.25	15.9	17.9	21.8	18.8
0.25-0.10	22.0	16.7	12.5	21.7
0.10-0.00	35.5	30.9	22.7	23.3
Mean weight-diameter .. *mm.*	0.504	0.680	0.791	0.721

* By weight.

TABLE 2

Effect of MCS treatment on aggregate distribution and mean weight-diameter of Ida silt loam from a corn plot in a 3-year rotation

AGGREGATE SIZE	AGGREGATE DISTRIBUTION	
	Untreated	0.2 per cent MCS
mm.	*per cent**	*per cent**
8.0 -2.0	6.7	18.0
2.0 -1.0	4.8	7.4
1.0 -0.5	7.8	9.2
0.5 -0.25	19.5	13.2
0.25-0.10	16.2	11.9
0.10-0.00	45.0	40.3
Mean weight-diameter *mm.*	0.541	1.044

* By weight.

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[5] Gish, R. 1947 Factors affecting the stability of soil aggregates. 1947 [Unpublished master's thesis. Copy on file Iowa State College Library, Ames.]

Clarion loam (table 3). To demonstrate the magnitude of the effects, again data are included in table 3 on untreated soil in continuous bluegrass.

The soil of table 1 was taken from a very badly eroded plot and was therefore not strictly comparable with the other two. Under similar conditions it would seem that the poorer soil received the greatest benefit in terms of water-stable aggregation. This is shown in table 4, where the results, in terms of mean weight-diameters, are listed for Clarion loam cropped in continuous corn, rotation corn, and rotation meadow.

TABLE 3

Effect of MCS treatment on aggregate distribution and mean weight-diameter of Clarion loam from a corn plot in a 3-year rotation, in comparison with an untreated soil from a continuous bluegrass plot

AGGREGATE SIZE	AGGREGATE DISTRIBUTION			
	Rotation corn plot			Continuous bluegrass plot untreated
	Untreated	0.2 per cent MCS	0.5 per cent MCS	
mm.	*per cent**	*per cent**	*per cent**	*per cent**
8.0 -2.0	6.7	20.9	24.8	31.1
2.0 -1.0	5.7	9.0	9.3	15.7
1.0 -0.5	14.1	13.7	12.8	14.0
0.5 -0.25	24.8	23.4	21.2	15.9
0.25-0.10	27.0	22.0	17.5	12.8
0.10-0.00	21.7	11.0	14.4	10.5
Mean weight-diameter..*mm.*	0.638	1.071	1.754	1.783

* By weight.

TABLE 4

Effect of MCS treatments on mean weight-diameter of the aggregate distributions of Clarion loam in various crops

	MEAN WEIGHT-DIAMETER		
	Untreated	0.2 per cent MCS	0.5 per cent MCS
	mm.	*mm.*	*mm.*
Continuous corn	0.223	1.071	1.754
Corn of corn-oats-meadow	0.638	1.286	1.523
Meadow of corn-oats-meadow	0.957	0.877	1.882

The question has been raised whether the ordinary technique of wet-sieving is a sufficient indicator of the stability of aggregates. Wilson, Gish, and Browning (7) advocated that the soil sample be shaken in water end-over-end in a 1000-ml. graduate a number of times before it is placed on the top screen of the nest of sieves used in wet-sieving analysis. The effect of the MCS treatment might possibly disappear or be reduced under such a severe treatment. To investigate this point, a determination was made of the mean weight-diameter of Marshall silt loam and Ida silt loam preshaken 50 times as described. The results are given in table 5.

The preshaking treatment diminishes the size of the aggregates, as expected, but the effect of the MCS treatment, except for the 0.2 per cent Marshall, is just as apparent and large as under standard conditions of determining aggregate distribution, as may be seen by comparison with tables 1 and 2.

TABLE 5

Effect of MCS treatments on mean weight-diameter of aggregate distributions of Marshall silt loam and Ida silt loam, pre-shaken 50 times

TREATMENT	MEAN WEIGHT-DIAMETER	
	Marshall silt loam	Ida silt loam
	mm	*mm*
Check	0.390	0.189
0.2 per cent MCS	0.383	0.303
0.5 per cent MCS	0.675	0.525

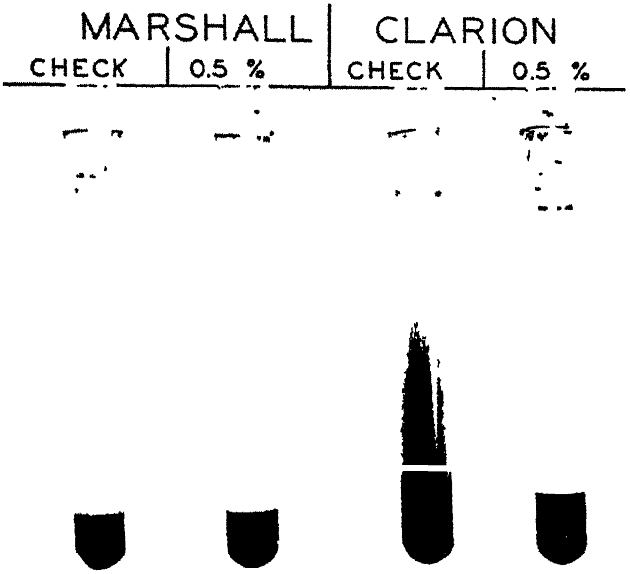

FIG. 1. TURBIDITY OF SOIL SUSPENSIONS 2 HOURS AFTER SHAKING

Untreated soil versus soil treated with 0.5 per cent methylchlorosilane.

A qualitative demonstration of the effects of MCS treatment was obtained by suspending treated and untreated soil in water and allowing the suspensions to settle. Figure 1 shows suspensions of two soils treated with 0.5 per cent MCS together with suspensions of untreated soils after settling for 2 hours.

The results of measurement of the liquid limit and the plastic limit on four soils are presented in table 6 as well as the plastic index and its decrease as the result of the treatment.

The MCS treatment decreases the plastic index consistently. The effect of the treatment is not so large as the effect on aggregation, but small changes in the plastic index appreciably affect the suitability of soil for construction purposes (1). The decrease in plastic index also indicates that soils would be more friable as result of treatment.

DISCUSSION

The significance of the effect of methylchlorosilanes on water-stable soil aggregation seems great from this first study. The action is, as appears from the data, particularly one of preserving the aggregates that are present in relatively dry soil against the slaking action of water, which could also be predicted from the nature of the compound used. Such action would tend to decrease suspension of soil in runoff water and decrease the sealing of the soil surface by disintegrated soil aggregates, both resulting in decreased erosion and increased infiltration capacity. Whether these effects will actually be found under field conditions is being investigated.

TABLE 6

Effect of MCS treatment on plastic indexes of four soil materials

	LIQUID LIMIT		PLASTIC LIMIT		PLASTIC INDEX		REDUCTION OF PLASTIC INDEX
	Check	0.5 per cent MCS	Check	0.5 per cent MCS	Check	0.5 per cent MCS	*per cent*
Marshall silt loam	43.4	39.6	26.2	25.6	17.2	14.1	19
Ida silt loam[1]	36.8	36.3	28.7	29.4	8.1	6.9	15
Mankato till	32.9	31.7	17.1	17.6	15.8	14.1	11
Edina subsoil	79.6	71.8	31.1	32.0	48.5	39.8	18

[1] Treated at a rate of 0.2 per cent MCS.

Another question that arises concerns the possible toxic or obnoxious effects of the treatment on soil or soil organisms. Data to clarify this point have been collected but will need extension before conclusions can be drawn.

The results obtained may throw more light on the question of water-stability of soil aggregates. Soil organic matter has consistently been found to contribute to water-stability. Most explanations for this observed phenomenon have stressed organic matter components that were sticky or that in some way bonded soil particles together. Perhaps the waterproofing organic matter components like fatty acids, fats, and waxes are more important for aggregate stability. The role of different crops and crop management systems in soil structure deterioration or improvement could be viewed from this standpoint also. Due cognizance must be taken of factors like fibrousness of root systems and bodies of soil microorganisms, but soil structure and its stability obviously have characters of more lasting nature than the presence of root systems or soil microorganisms.

SUMMARY

Air-dry soil was exposed to the fumes of a mixture of two methylchlorosilanes under reduced pressure. It was found that treatment of different soils, with widely varying degrees of water-stable aggregation, at a rate of 0.2 per cent and 0.5 per cent by weight of the soil increased the water-stability. Measured as the value of the mean weight-diameter, the aggregation of the soils treated was increased between 50 and 600 per cent, depending on rate of treatment and original condition of the soil.

The plastic index of several soils was found to be decreased as a result of the treatment. Practical implications of the experimental results for reducing surface sealing, decreasing erodibility, and increasing stability of earth structures are indicated.

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EFFECTS OF PARTICLE SIZE AND TEMPERATURE ON THE PERMEABILITY OF SAND TO WATER

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Received for publication January 30, 1950

In 1945 information was published (14) on factors in permeability changes of soil and inert granular material. Other information obtained on the effect of particle size and of temperature on permeability is here presented.

The effect of texture on permeability is well recognized, presumably actual variations being the results of differences in pore size (2; 7; 9, pp. 159–160; 10). Size separates of silica sand were taken with an elutriator. The separates were thoroughly acid-cleaned and washed and then carefully and uniformly packed in permeameters. Permeability was determined with recently boiled distilled water. Permeability increased until all entrapped air had been dissolved, and then became constant. Sizes of the separates were determined by microscopic examination of samples. The work was done in a room kept constantly at 20°C. Following are the results, with permeability as defined in table 1:

TABLE 1

Saturation apparent velocities (v) *at unit gradient and permeabilities* (k) *of inert sand separates and of one soil at varying temperatures after entrapped air dissolved* (*in recently boiled distilled water with 50 ppm.* $HgCl_2$ *added*)

Permeability defined as $k = v\eta / i\eta_s$ where v = cm.³ flow per hr./total cross-sectional area of permeameter in cm.², i = hydraulic gradient, η_s = viscosity of water at 20°C. in centipoises, η = actual viscosity of water in centipoises

Room at constant temperature until permeability constant, then room temperature changed in sequence left to right. Uniform compaction, June 1944

AVERAGE PARTICLE DIAMETER	BULK DENSITY	REAL DENSITY	TEMP. 35°C.		TEMP. 25°C.		TEMP. 15°C.		TEMP. 6°C.		TEMP. 35°C.	
			v*	k	v*	k	v*	k	v*	k	v*	k
μ	gm./cm.³	gm./cm.³	cm./hr.	cm./hr.	cm./hr.	cm./hr.	cm./hr.	cm./hr.	cm./hr.	cm./hr.	cm./hr.	cm./hr.
360	1.48	2.60	558	405	444	398	346	393	263	386	534	388
250	1.47	2.62	200	145	165	148	128	145	100	147	196	142
180	1.45	2.63	116	84	90	81	71	81	54	79	110	80
110	1.43	2.64	50	36	41	37	31	35	24	35	49	36
Indio.... loam†..	1.32	2.83	0.89	0.65	0.78	0.70	0.63	0.72	0.50	0.73	1.00	0.73

* At unit gradient.

† Permeability at a constant temperature was somewhat variable. The permeabilities shown were approximate averages.

Av. particle size of separates (μ)	*k(cm./hr.)*
500	875
360	368
250	102
180	82
110	28

Those who have worked with the permeability of relatively inert sands (5, 8, 11, 15) have generally concluded that permeability appears to vary more or less in accordance with the viscosity of the water. Others, working with soils (4, 6, 12), conclude that the viscosity effect is minor because of the other variables involved. Bouyoucos (3) found percolation rates to increase with temperature up to 30°C. and then to decrease. Moore (13), working with soils during their initial wetting, found somewhat of a viscosity effect from 5° to 30°C. but found a rapid increase in permeability from 30° to 35°C. With soils, microorganisms and the effect of temperature upon their activity can mask direct viscosity effects (1). The runs reported in table 1 were therefore made under presumably sterile conditions. Size separates were of the same stock supplies as were used in runs previously discussed, although the packing technique varied.

CONCLUSIONS

With size separates of acid-cleaned and washed silica sand, uniformly packed, saturated permeability appeared to be an exponential function of particle size.

With the same inert sand, under conditions where there could be no activity of microorganisms, variation of saturated permeability with temperature was wholly a viscosity effect.

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CAUSES OF DIURNAL FLUCTUATIONS OF TENSIOMETERS

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Received for publication March 9, 1950

Large diurnal fluctuations of tensiometers have been observed by investigators who have used these instruments to measure soil moisture tension or the security with which water is held by the soil. Richards (9) recently provided an excellent review of operating characteristics and usefulness of these instruments under field, greenhouse, and laboratory conditions. A problem sometimes associated with behavior of tensiometers but which may not always be a serious factor is a diurnal tension swing that does not appear entirely related to changes in soil moisture content. Richards has pointed out that "tensiometer readings are subject to a daily variation that has not yet been fully studied and explained. It may be due in part to change in moisture content of the soil because, for field installations, readings generally increase during the afternoon when the transpiration load is greatest. The diurnal swing is greatest when the cup is near the surface and sometimes may be observed in absence of moisture extraction by plant roots."

This paper is concerned with the extent of diurnal fluctuations of tensiometers on coarse-textured mesa soils, the cause of these fluctuations, and a discussion of implications involved in use of the instruments.

REVIEW OF LITERATURE

Large fluctuations in the reading of a tensiometer attributed to diurnal temperature changes have been reported by Richards *et al.* (5). This investigation was made in Marshall silt loam soil at Clarinda, Iowa. A porous cup connected to a mercury column was installed in the center of a 1-quart can of soil, which was carefully sealed to prevent moisture losses. Atmospheric pressure in the soil air was provided by a small vent. When the apparatus was fully exposed to the summer sunshine, a maximum variation of about 140 cm. of water as indicated by the mercury manometer was noted. A decrease in the manometer reading occurred as the soil temperature increased, and conversely a decrease in soil temperatures resulted in an increase in manometer reading. Further evidence of daily fluctuations was observed in the use of flow gauges that measured vertical flow of soil moisture at depths of 2 and 6 inches. It is reported that "diurnal fluctuations in the flow rate curves are exaggerated by, if not caused by, the temperature fluctuations in the soil." The related effect of temperature on the capillary tension of the soil water was offered as a possible explanation.

Richards and Neal (4) obtained tensiometric records on a vacuum gauge which indicated a variation of approximately 176 and 148 cm. of water at depths of 6 and 12 inches respectively. They found that the capillary tension minima occurred near 6:00 a.m., and the maxima occurred between 7:00 and 9:00 p.m. The period of increasing tensions corresponded almost exactly to the hours of sunshine on the plot.

Large daily fluctuations of tensiometer readings have also been noted by Olmstead[2] at

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[1] Contribution from the Yuma Mesa Soil and Crop Laboratory, Yuma, Arizona. The authors acknowledge the assistance of J. S. Salyer in collecting data and of C. D. Converse in planning this study.

[2] Unpublished data—Permission to use data obtained from author by personal communication.

Hays, Kansas, where instruments were installed at 3, 6, 9, and 16 inches in fallow soil of a wheat-fallow rotation. The magnitude of the fluctuations decreased with depth, and at 6 inches the tension varied as much as 360 cm. of water in a 24-hour period. Olmstead found that he could vary at will the moisture tension as indicated by the mercury manometer by simply changing the temperature of the soil mass; that is, when the soil was warmed, the tension dropped, and when the soil was cooled, the tension rose.

Diurnal variations in tensiometer readings as great as 500 cm. of water were observed by the authors[3] where instruments were installed in a guayule nursery at Indio, California in 1943. In this instance the soil type was Coachella loamy sand and the crop was irrigated by a sprinkler system.

Moore (3) has studied the effect of temperature on the pressure potential, retension, and infiltration rate of soil moisture. In three Yolo soils at three different moisture contents, he found rather large effects of temperature on the pressure potential without having thermal gradients. When soil temperatures were rapidly changed from one stage to another "it generally required less than 24 hours for significant temperature gradients in the soil to disappear. The corresponding pressure potentials also changed rapidly following a change in bath temperature, but this phase of rapid pressure change was followed by a longer period of slow drift before becoming constant." No mention was made of the magnitude of the changes in pressure potential which occurred during the equilibrium period.

A tensiometer tends to act like a thermometer when the volume of water in the tensiometer changes. An increase in volume of water lowers the tension reading, and conversely, a decrease in volume causes the mercury to rise. This effect has been reduced (2, 5) by restricting the water capacity of the instrument. It should be emphasized, however, that fluctuations from this cause tend to minimize the magnitude of the daily variations noted; that is, increased temperatures cause an increase in volume of water in the tensiometer and a subsequent lowering of the mercury column. As pointed out above, increase in temperature causes an increase in manometer reading.

EXTENT OF DIURNAL FLUCTUATIONS

The investigation was conducted on the Yuma Mesa, near Yuma, Arizona, in the spring and summer of 1949. The soils in this area are predominately in the Superstition series and range in texture from loamy fine sand to sand. Figure 1 shows the desorption curves of soil at various depths taken from the experimental site. In this soil most of the water available to plants is held between tensions of 100 cm. (approximately field capacity) and 500 cm., or 0.5 atmosphere. Diurnal fluctuations of temperature are often as much as 45°F., and maximum temperatures of 110 to 120°F. are not uncommon. Low humidity and high transpirational losses by plants add to the difficulty of maintaining an ample moisture reserve in soils of low water-holding capacity.

Observations were made on 155 tensiometers equipped with mercury manometers as pressure indicators. These instruments were being used in an alfalfa moisture and fertility experiment and were set to record soil moisture tension at the cup at depths of 6, 12, 18, 24, 36, 48, 72, 96, and 120 inches. The tensiometers were constructed as described by Richards (8, 9).

To determine the extent of the tension swing and the time when maximim and minimum readings occurred, successive records were taken on April 21–22 for 23 hours. The alfalfa was irrigated on April 15 and cut on April 18, three days before these observations were made. Figure 2 shows the minimum tension values occurred between 6:00 and 8:00 a.m., and maximum values between 7:00 and 9:00 p.m. This is in agreement with the observations by Richards and Neal (4) and by Olmstead.[4] Further examination of these data reveal several noteworthy features, namely (*a*) fluctuations in tension occur to depths of 36 and 48 inches, the magnitude of the variations decreasing with depth. At 72 and 120 inches no appreciable changes are noted; (*b*) the drop in tension which occurs between 7:00 and 9:00 p.m. closely approximates the time when soil temperatures at the 6-inch depth begin to decrease and lags about 4 hours behind a decline in air temperatures; and (*c*) volume changes of water in the tensiometer system are reflected by a drop in the mercury column as the sun rose (6:02 a.m.) and air temperatures increased. The magnitude of the fluctuation in centimeters of water at the 6-inch depth, which ranges from a minimum of 98 to a maximum of 474 and back to a minimum of 74 within a 23-hour period, raises a question as to whether the recorded tensions indicate actual soil moisture conditions. This would also apply to tensiometers at depths of 48 inches or less.

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[3] Unpublished data.

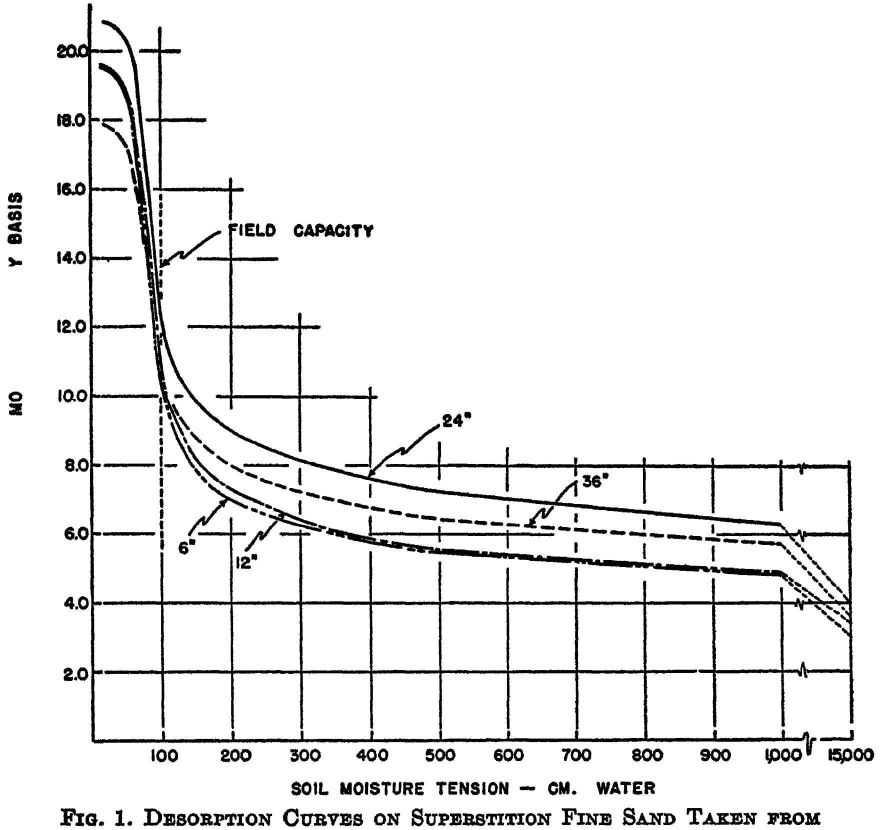

FIG. 1. DESORPTION CURVES ON SUPERSTITION FINE SAND TAKEN FROM EXPERIMENTAL SITE ON THE YUMA MESA NEAR YUMA, ARIZONA

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[4] Unpublished data.

A second series of tensiometric records were taken about 2 weeks later, from May 5 to 10, at the same site to determine the magnitude of day-to-day changes of tension values over one irrigation cycle. The alfalfa meanwhile had reached a height of 12 inches and had been irrigated one day prior to the time these observations began. The tensiometers were read at 8:00 a.m., 2:00 p.m., 8:00 p.m., and 2:00 a.m. and, as previously noted, included times when maximum and minimum tensions would be expected. These data are illustrated in figure 3. The magnitude of the daily variations at 6, 12, and 24 inches increases the first 2 or 3 days and decreases again as the upper tension limit of the instrument is approached. The tensiometers at 36 and 48 inches reflect a gradual increase in periodic fluctuations where tensions did not exceed 157 cm. of water. The maximum daily variation in moisture tension occurred on May 6–7 at the 6-inch depth, when the tension in centimeters of water rose from 138 to 594 and dropped to 146 the next morning. It will again be noted that the diurnal fluctuations decrease in magnitude with depth and virtually cease at 72 inches.

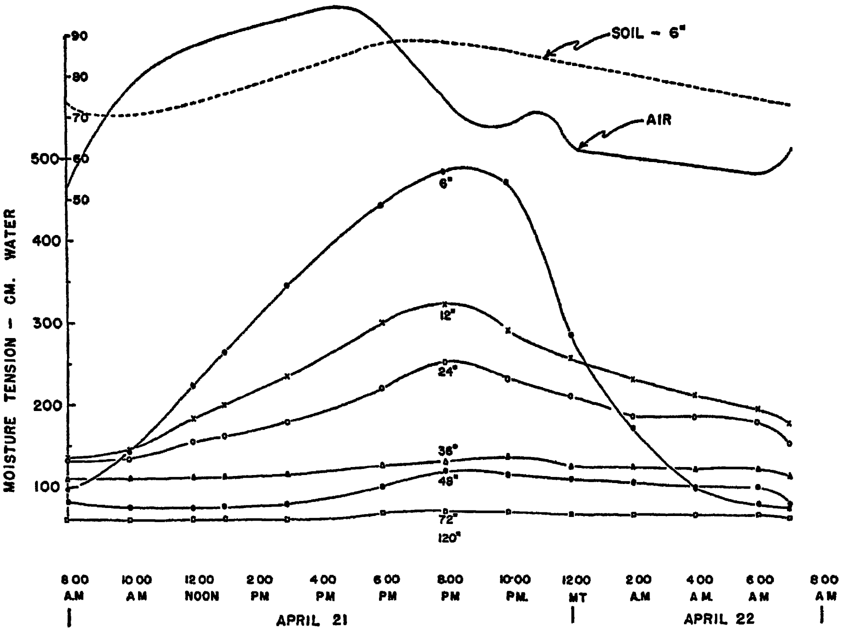

FIG. 2. PROGRESSIVE CHANGE IN TENSION RECORDED DURING 23-HOUR PERIOD BY TENSIOMETERS INSTALLED AT VARIOUS DEPTHS. SOIL AND AIR TEMPERATURES ARE ALSO SHOWN

CAUSES OF DIURNAL FLUCTUATION

It is apparent from earlier investigations cited that diurnal fluctuations of tensiometers are in some manner associated with temperature changes. As previously noted, the relatively large diurnal fluctuations which occur cannot be attributed to the variations in manometer readings caused by volume changes of the water in the tensiometer system. Fluctuations that arise from this cause are opposite in direction and thus tend to minimize the daily variations observed. The question was raised as to whether the effect of air temperature changes might create enough of a temperature gradient between the porous cup and the surrounding soil to cause a gain or loss of water from the cup through vapor transfer and condensation. It seemed likely that if the metal portion of the instrument to which the porous cup is attached was exposed to the cool night air, radiation of heat from the metal would occur more rapidly than from the soil. If this were true, it would follow that a temperature gradient from the cup to the soil would exist, and under these conditions diffusion of water vapor from the soil to the cooler porous cup surface would be expected. Then water that condensed at the air-water interface of the porous cup would enter the cup, since water in the tensiometer system would be under tension. Obviously, this would cause a decrease in the manometer reading at a time when air tem-

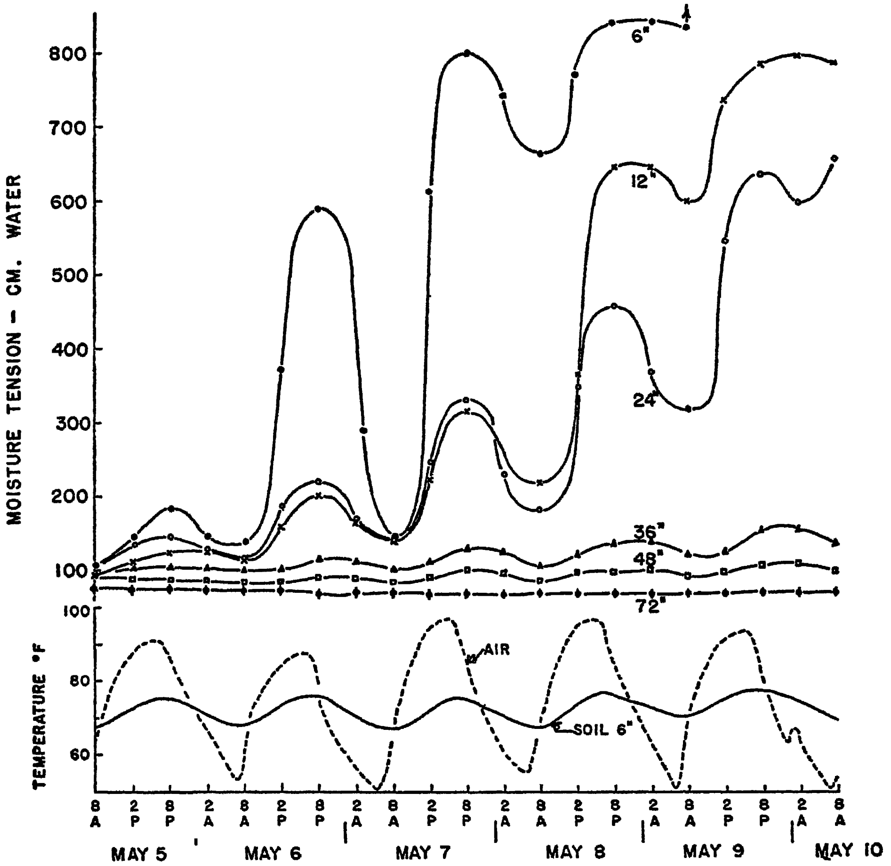

FIG. 3. DAY-TO-DAY FLUCTUATION OF TENSIOMETERS INSTALLED AT VARIOUS DEPTHS. SOIL AND AIR TEMPERATURES ARE INDICATED IN LOWER GRAPH.

peratures decreased and would be in the direction that major fluctuations have been observed. The reverse situation could cause the mercury in the manometer to rise by vapor transfer from the cup to the soil when the temperature gradient is in the direction of the porous cup. Such would be the case when daytime air temperatures rose and the metal portions of the instrument became warmed while the soil remained relatively cool.

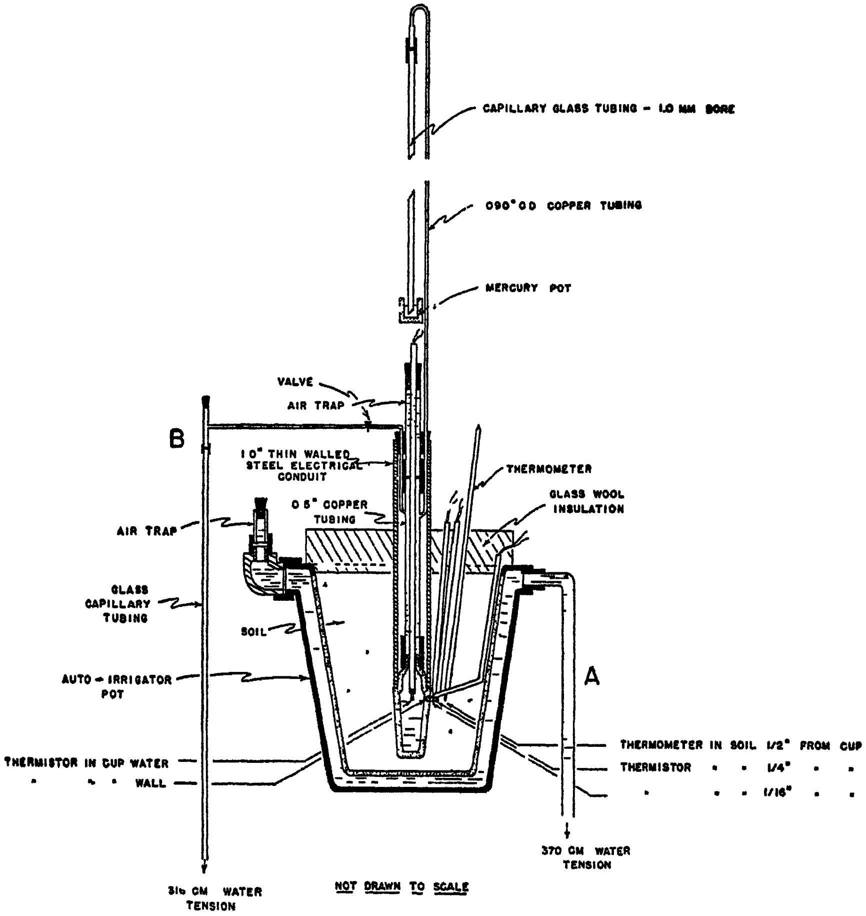

FIG. 4. DIAGRAM OF EXPERIMENTAL SET-UP USED TO DETERMINE CAUSE OF DIURNAL FLUCTUATION OF TENSIOMETERS

Arrangement of auto-irrigator pot, tensiometer, and thermistors is shown. Water column (A) is connected to auto-irrigator pot, and water column (B) to tensiometer system.

The validity of this theory was checked with the experimental set-up shown in figure 4. Constant soil moisture tension in Superstition fine sand was obtained with an auto-irrigator pot (6, 7). A standard type tensiometer was placed in the pot with the porous cup in the center of the soil mass $\frac{3}{4}$ inch from the bottom. The distance from the center of the cup to the soil surface was $5\frac{1}{2}$ inches. Glass-wool insulation 2 inches thick was placed on top of the soil and around the tensiometer to reduce evaporation and temperature variation at the soil surface. Temperature measurements of the water inside the porous cup, the cup wall, and the soil $\frac{1}{16}$ inch and $\frac{1}{4}$ inch from the cup were made with 14B type thermistors (1). Soil temperatures $\frac{1}{2}$ inch from the cup were obtained with a thermometer accurate to 0.1°C. The thermistors and thermometer were placed $\frac{1}{4}$ inch below the point where the cup was attached to the metal conduit. A hole $\frac{1}{16}$ inch in diameter drilled $\frac{1}{16}$ inch deep into the cup wall provided a suitable cavity in which a thermistor could be imbedded for the measurement of cup temperature. A temperature change of 0.005°C. was measurable with these instruments.

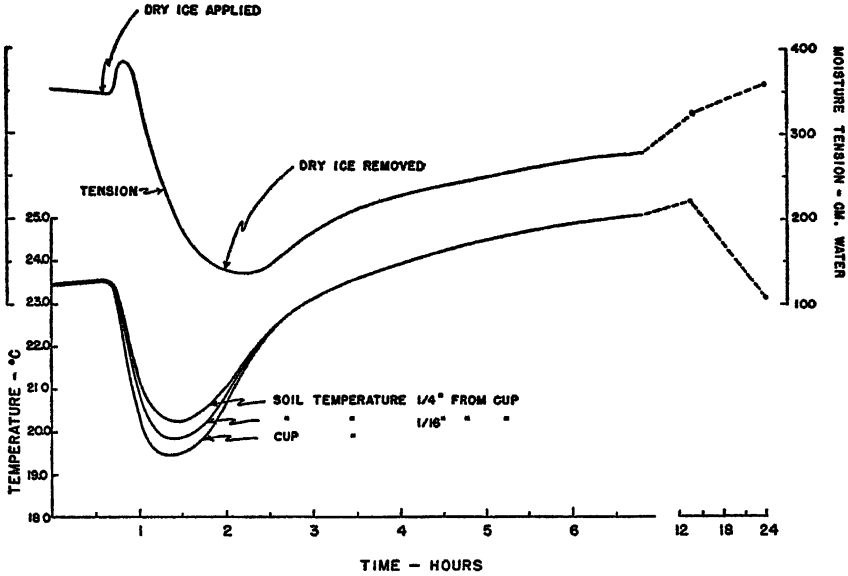

FIG. 5. EFFECT OF CHANGE IN TEMPERATURE ON TENSIOMETER READING WHEN PART OF INSTRUMENT ABOVE INSULATION IS COOLED

Note decrease in tension during period when temperature gradient existed from cup to soil.

When the auto-irrigator pot, the soil, and the tensiometer were essentially in equilibrium with a tension of 370 cm. of water, powdered dry ice was placed around the metal conduit of the tensiometer above the insulated layer which covered the soil in the auto-irrigator pot. The progressive changes in the tensiometric reading with temperature are shown in figure 5. In the half hour before application of the dry ice, the tension decreased slightly while soil and cup temperatures increased slightly. When the dry ice was applied to the tensiometer, a rapid rise of mercury in the manometer equivalent to 32 cm. of water resulted. This apparent increase in tension was attributed to volume change of water in the tensiometer system. As radiation of heat from the metal tube and porous cup progressed, a temperature gradient from the cup to the soil was established, that is, the cup temperature was lower than that of the surrounding soil mass. As long as this temperature gradient was maintained, the mercury in the manometer continued to drop. The difference in temperature between the cup and soil $\frac{1}{16}$ inch from the cup at the time the mercury began to drop was 0.25°C., and the maximum differential attained 24 minutes later was 0.45°C. When the dry ice was nearly dissipated, the portion that remained was removed. At this time the tensiometer indicated a tension of 136 cm., a maximum drop of 244 cm. of water. After removal of the dry ice, the temperature gradient decreased progressively as the temperatures at all points simultaneously increased. When the temperature gradient approached 0, the mercury in the manometer began to rise. Two hours and 50 minutes after the experiment was started, the temperature of the cup and the soil was exactly the same. The rise in tension continued, and after 24 hours was the same as the initial reading taken before the dry ice was applied.

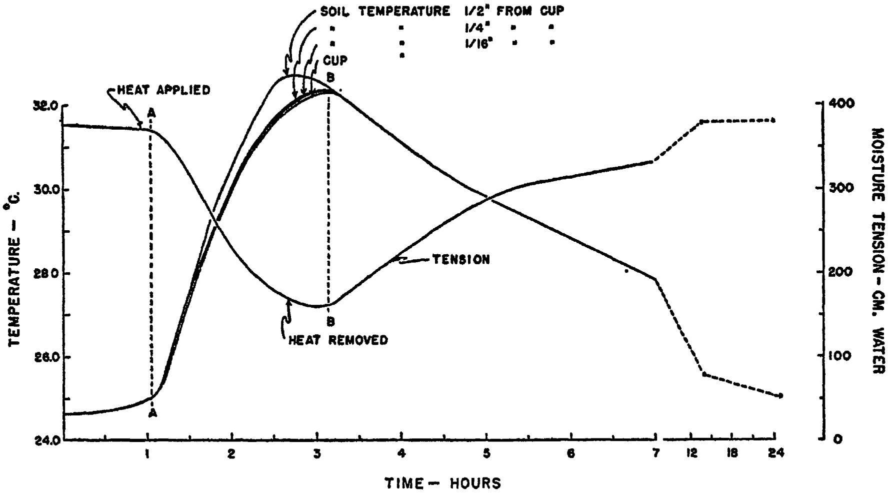

FIG. 6. EFFECT OF CHANGE IN TEMPERATURE ON TENSIOMETER READING WHEN SOIL MASS AROUND TENSIOMETER CUP IS WARMED

Note decrease in tension during period when temperature gradient existed from cup to soil.

The same effect was demonstrated when the temperature of the soil was raised by circulation of warm water through rubber tubing wrapped around the outside of the auto-irrigator pot. The part of the instrument above the insulation remained exposed to room temperature. Figure 6 shows that a temperature gradient from the cup to the soil resulted soon after heat was applied to the auto-irrigator pot. A simultaneous lowering of the mercury in the manometer was noted at the time the cup temperature dropped 0.010°C. lower than the soil temperature $\frac{1}{16}$ inch from the cup and 0.050°C. lower than the soil temperature $\frac{1}{4}$ inch from cup. The mercury continued to drop until the heat was removed and the temperature gradient again approached 0. Within 12 hours the mercury gradually rose to the approximate value noted before heat was applied. A maximum decrease of 217 cm. of water was noted during the time a temperature gradient existed.

It is evident from these laboratory results that diurnal fluctuation of tensiometers is the result of a temperature gradient between the porous cup and the soil brought about by temperature changes. Direct evidence that water collects at the cup surface and enters the tensiometer systems has been lacking. A simple alteration of the apparatus in figure 4 established that this actually happens. Capillary copper tubing B was soldered into the air trap of the tensiometer and suspended to a depth of 316 cm. in a well. The valve inserted into the line as shown in the diagram (fig. 4) permitted the tensiometer system and the suspended tube to be charged with water. When the air bubbles in the line B and in the tensiometer were entirely removed, the valve was closed and the tensiometer was permitted to reach equilibrium with the soil moisture. The lower end of tube B was placed in water to prevent evaporation. Capillary glass tubing was used in the vertical section to detect any air bubbles that might appear in the line.

When equilibrium was attained in the system, the tensiometer recorded 376 cm. of water tension which was approximately equal to the column of water A (fig. 4) connected to the auto-irrigator pot. If the valve in line B had been opened at this time, the water contained in this column would have been drawn into the tensiometer, since the tension of the water in the tensiometer system was 60 cm. greater than in line B. Powdered dry ice was then placed around the tensiometer in a manner previously described. After the initial rise of the mercury in response to volume changes of the water with temperature, the tension began to drop. When the tensiometer recorded a tension of 300 cm. of water, the valve in line B was opened and, as would be expected, the mercury immediately indicated a tension of 316 cm. of water in response to water column B. When the valve in line B was opened, flow of water at the lower end of this line was observed. In a cooling period of 50 minutes, 0.25 cc. of water had been collected. This was more than the calculated amount required to lower the mercury an equivalent of 300 cm. of water tension. Since the soil moisture tension was at 376 cm. of water, it was concluded that water collected at the end of column B, which was 316 cm. high, would of necessity be that which had condensed on the porous cup during the cooling period.

Further evidence that diurnal fluctuation of tensiometers is caused by temperature change as it affects vapor movement to and from the porous cup can be seen in the inset of figure 7. These data were obtained from four 6-inch tensiometers in alfalfa. Each curve represents the average of two tensiometer readings taken at 8:00 a.m., 2:00 p.m., and 8:00 p.m. from July 27 to August 2. The arrow indicates the point where two tensiometers represented by the broken line were raised $\frac{1}{2}$ inch to break contact between the porous cup and the soil. When the tensiometers were raised this distance, the taper of the cup provided a clearance of approximately $\frac{1}{16}$ inch between the cup and the soil. Although the magnitude of the fluctuations of the pair represented by the solid line were

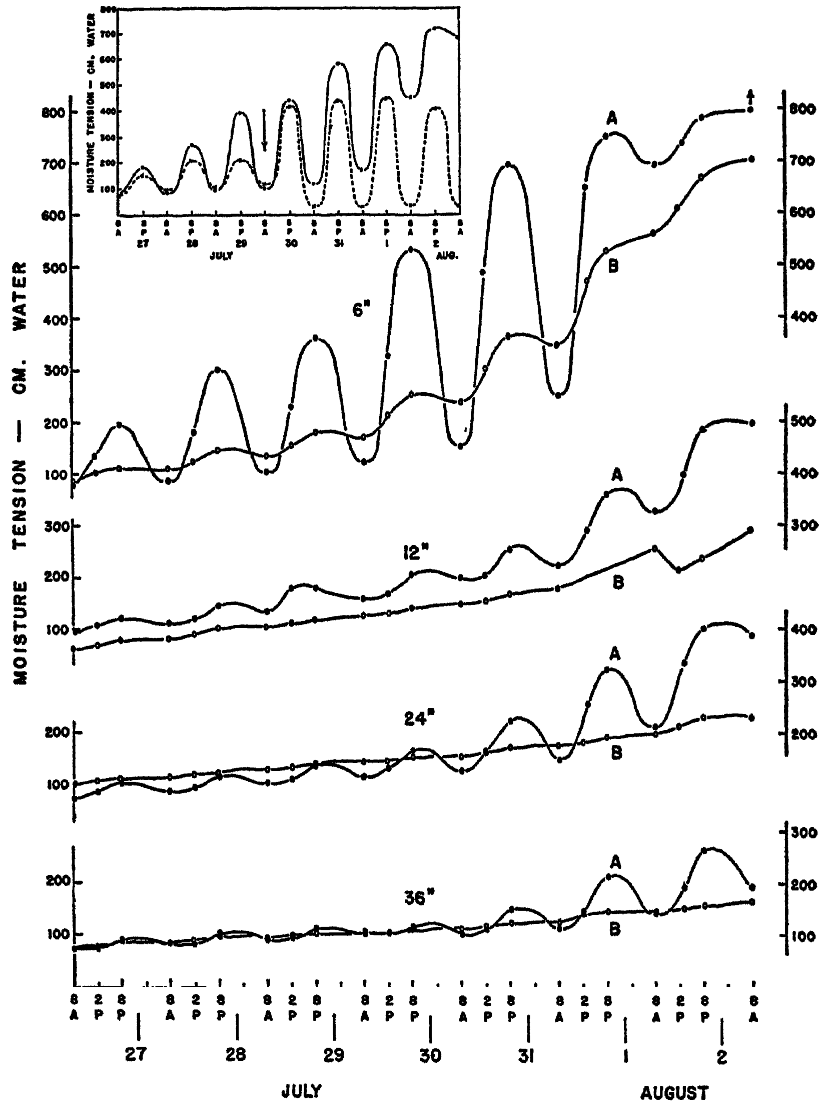

FIG. 7. TENSIOMETRIC DATA SHOWING COMPARISON OF STANDARD TYPE TENSIOMETERS (A) WITH TENSIOMETERS WITHOUT METAL SUPPORT (B) AT DEPTHS OF 6, 12, 24, AND 36 INCHES

Insert shows diurnal fluctuations of standard type tensiometers installed to a depth of 6 inches. Manometer readings indicated by broken line to the right of arrow were obtained after these instruments were raised ½ inch to break contact between porous cup and soil. Solid line represents variations in manometer readings where porous cup remained in contact with soil.

somewhat greater, a typical tension swing of all tensiometers was apparent for the first 3 days. When contact between the cup and the soil was broken at 8:00 a.m. on July 30, the mercury in the tensiometers, shown by the broken lines, fluctuated daily between a maximum and a minimum of approximately 425 and 25 cm. of water respectively. The behavior of those which remained in contact with the soil over the same period was generally the same as previously noted. These data indicate that diffusion of vapor to the cup during the night and away from the cup during the day occurs freely even though the soil becomes progressively drier. Where the porous cups were in contact with the soil, apparently part of the water that collected at the cup was absorbed by the soil when the moisture tension of the latter increased with time and probably accounts for the decrease in magnitude of the fluctuations in the drier range of soil moisture.

Exposure of the metal parts of tensiometers with standard type construction to relatively warm days and cool nights and the effect which these temperature changes might have on the temperature gradient between the porous cup and the soil have been pointed out. Whether the diurnal fluctuations could be reduced by a change in tensiometer design was determined by construction of four instruments that eliminated the air trap and the metal support to which the porous cup was attached. This was accomplished by the underground extension of two capillary copper tubes from the porous cup to a point 10 feet away. One tube served to charge the system with water and eliminate air bubbles, while the other was connected to a mercury manometer. These instruments were placed 6 inches away from standard type tensiometers in alfalfa at depths of 6, 12, 24, and 36 inches. The extended copper tubes were buried 8 inches deep to minimize any temperature change at the cup.

A comparison of the results obtained with the two types of instruments between July 27 and August 2 are shown in figure 7. A typical diurnal tension swing was recorded at all depths with the tensiometers of standard construction (A). Fluctuation of the tensiometers without the metal support (B) was limited to the 6-inch depth, and here the magnitude of the variations was considerably less. The one irregularity in curve B at the 12-inch depth was attributed to an air-leak which developed in the tensiometer system. It appears from these data that temperature variation and vapor transfer at the cup are facilitated by heat radiation from the metal tensiometer support and the air trap.

DISCUSSION

In view of the data presented, a number of questions arise that concern the use of tensiometers. Foremost among these is the time of day when tensiometers should be read. Richards (9) suggests that, "The effect of the diurnal fluctuations on the readings of field instruments can be minimized by making the readings at the same time of day, preferably in the morning, so as to follow a period of slow temperature change." The data in figure 7 substantiate this statement if the soil moisture tension indicated by the tensiometers without metal supports is assumed correct. Minimum tension values of standard tensiometers observed in the morning were generally in agreement with the buried tensiometers where diurnal fluctuations had apparently been eliminated below the 6-inch depth. When, however, soil moisture samples taken daily at 8:00 a.m. and

8:00 p.m., at the various cup depths, were related to tension values as determined from desorption curves on the composited soil samples, indications were that the soil moisture tension was greater than that shown by the maximum readings noted at 8:00 p.m. These data were preliminary, and more study is needed to clarify this point. Obviously, however, under conditions of the Yuma Mesa, it is not certain when tensiometers indicate actual soil moisture conditions, especially in the upper 24 inches of soil. The problem is complicated by volume changes of the water in the instrument. It was found that an immediate rise in air temperature caused the mercury in the manometer to drop about 6 cm. of water for each degree C. change in temperature. How much of the rise in mercury can be attributed to vapor transfer from the cup to the soil or to equilibrium established by actual film contact and flow over the soil particles is not known. The possibility that the soil moisture content varies from day to day as a result of vapor movement in the soil itself should not be overlooked. There are indications that temperature variations with seasonal changes affect the magnitude of the fluctuations. During the current summer months when maximum temperatures ranged from 105° to 115° and minimum temperatures exceeded 80°F., fluctuations were much less pronounced than those observed in spring and fall. It also seems likely that, when the water collects at the cup surface as air temperatures drop, the soil moisture surrounding the cup might be supplemented. This could cause lower tensiometric values especially in coarse-textured soils where a small change in moisture content on the steep part of the desorption curve causes large differences in tension.

The complexity of the problem indicates that it would be difficult to read tensiometers at a time that would represent the actual moisture conditions in the upper 1- or 2-foot layer of soil. From data obtained, one would suspect that tensiometers register the correct soil moisture tension twice a day, once during the period when the mercury rises in the manometer and again in the period when the mercury falls. Until further evidence is presented, it seems advisable that tensiometers should be read in the morning.

It should be emphasized that the above discussion applies to soil and temperature conditions on the Yuma Mesa. Evidence of the extent of diurnal fluctuations in other areas has been previously cited but is too limited for critical evaluation. It is, nevertheless, important that those who make use of tensiometers be aware of the fact that where diurnal fluctuations do occur, erroneous interpretation of data is possible. This is particularly true where tensiometers are used to study soil moisture movement, field capacity, or moisture reserves. Diurnal fluctuation of tensiometers used to anticipate the need for irrigation on heavier textured soils may not be serious, since the portion of the available range of moisture included is considerably less than for coarser textured soils.

As previously indicated, an attempt has been made to change the design of tensiometers which minimized fluctuation due to volume change of the water in the system. With proper selection of materials, perhaps further progress can be made toward designing a tensiometer which is less sensitive to changes in temperature that cause diurnal fluctuation.

SUMMARY

Large diurnal fluctuations of tensiometers were noted under soil and climatic conditons of the Yuma Mesa near Yuma, Arizona, during the 1949 season. Observations were made on 155 standard-type instruments with mercury manometers installed in alfalfa to depths of 6, 12, 18, 24, 36, 48, 72, 96, and 120 inches. It was found that minimum tension values occurred between 6:00 and 8:00 a.m. and maximum values between 7:00 and 9:00 p.m. Fluctuations were noted to depths of 48 inches, the magnitude of the variations decreasing with depth. No appreciable change in tension occurred below 72 inches. Daily variations in tension of 350 to 400 cm. of water at the 6-inch depth were common.

Day-to-day changes in manometer readings indicated a progressive increase in the magnitude of daily fluctuations the first 2 or 3 days. The extent of these variations later decreased as the soil became drier and the upper tension limit of the instrument was approached.

Laboratory studies under conditions of constant soil moisture tension have shown that diurnal fluctuations of tensiometers occur when a temperature gradient exists between the porous cup and the soil. Temperature changes at the cup were attributed to heat radiation from the metal support and the air trap to which the porous cup is attached. When the tensiometer was cooled, a temperature gradient from the cup to the soil was established. As water vapor diffused from the soil to the cooler porous cup surface, condensed vapor entered the tensiometer system and caused the mercury in the manometer to drop. As the temperature gradient approached 0, the mercury rose to the initial value within 12 to 24 hours.

The complexity of the problem as related to the time of day when tensiometers should be read is discussed.

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PROFILE STUDIES OF NORMAL SOILS OF NEW YORK: III. PHYSICAL AND CHEMICAL PROPERTIES OF BROWN FOREST AND GRAY-BROWN PODZOLIC SOILS

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Received for publication February 25, 1950

This article deals with physical and chemical properties of soils representing (*a*) intergrades between brown forest and gray-brown podzolic soils, (*b*) gray-brown podzolic soils with high base status, and (*c*) gray-brown podzolic soils depleted of bases in the upper horizons. These three soil conditions are segments of a geographic sequence of profiles on calcareous glacial drift in western New York. They have been described in the first article of this series of papers (2), where it was suggested that they are analogous to successive stages in the development of gray-brown podzolic soils on calcareous material in this region.

EXPERIMENTAL METHODS

Ten sites were selected in unpastured wooded areas of Ontario County, New York, to provide profiles representative of the complete acidity range of well-drained soils on glacial till dominated by limestone. Seven of the ten profiles were within the range of the gray-brown podzolic Honeoye series; three were intergrades between brown forest and gray-brown podzolic soils, tentatively known as the Fenner series but normally undifferentiated from Honeoye soils in mapping because of small extent and erratic occurrence in this area.

The profiles were sampled by genetic horizons delineated on the sides of freshly dug pits. The samples were air-dried, ground in a mortar with a rubber-tipped pestle, and passed through a 2-mm. sieve. The fractions passing the sieve were stored in air-tight glass bottles for analyses.

Mechanical analyses were made in duplicate by the method of Olmstead et al. (15). Bulk densities were determined by the paraffined-clod method. The pH values were determined potentiometrically with the glass electrode, using a 1:1 suspension as suggested by Peech *et al.* (16).

The cation-exchange capacities were determined by the method of Peech *et al.* (16). Five grams of soil were used in each determination, and Gooch crucibles were used for the leaching. All extracts, except those from the C horizon, were nesslerized, and the cation-exchange capacities were determined colorimetrically. Exchange capacities of the calcareous C horizons were determined by direct distillation using the Kjeldahl method for ammonia.

Organic matter determinations were made by the modified Walkley method proposed by Peech *et al.* (16).

Total chemical analyses of the material finer than 2 mm. were made according to the method proposed by Robinson (18) with the exception of the determinations of phosphorus, sodium, and potassium. Sodium and potassium were determined by the J. Lawrence Smith method, except that the sinter cake was dissolved in HCl, and sodium and potassium were determined with the Beckman flame photometer using standard solutions with the same calcium contents as the unknowns. Total phosphorus was determined, by the Dean and Deemer modification of the Schricker and Dawson method, as given by Bray and Kurtz (1), on an aliquot of the solution used for the manganese determination.

TABLE 1

Mean particle-size distribution and standard deviations of genetic horizons of profiles grouped on the basis of acidity of the A horizons

In per cent

HORIZON	SAND		SILT		TOTAL CLAY		0.2μ CLAY	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Group 1, 3 profiles								
A_1	44.32	1.51	37.77	4.38	17.90	2.86	9.85	3.04
A_2	46.95	0.56	35.60	3.51	17.43	2.98	9.80	1.39
B_2	49.05	7.38	31.75	4.21	19.40	3.10	10.68	7.63
B_3	52.48	5.71	31.08	3.89	16.39	2.97	8.19	4.91
C	48.04	1.67	39.57	3.84	12.41	2.75	4.32	2.07
Group 2, 4 profiles								
A_1	37.87	2.33	44.54	7.15	17.33	5.77	5.99	1.45
A_{21}	38.10	4.36	46.36	4.75	15.57	2.43	5.40	2.47
A_{22}	42.84	7.89	40.84	4.24	16.32	4.33	6.60	1.25
B_{21}	38.96	2.56	35.01	1.64	25.74	3.95	11.64	3.61
B_{22}	37.24	7.48	35.38	2.90	27.52	4.83	16.81	6.05
B_3	40.02	1.97	37.35	3.40	22.25	5.90	12.87	3.24
C	41.09	7.49	43.33	5.38	15.70	7.33	6.35	3.76
Group 3, 3 profiles								
A_1	51.09	1.45	35.78	0.67	12.73	1.74	4.06	0.27
A_{21}	54.85	4.49	32.74	3.29	12.61	1.32	3.36	1.05
A_{22}	58.39	6.23	29.70	4.21	12.10	2.28	2.56	0.67
B_{21}	61.17	6.67	23.88	1.44	14.97	5.24	6.61	6.07
B_{22}	52.92	3.73	25.79	0.37	21.51	3.51	10.69	5.40
B_3	57.93	3.09	26.29	1.54	15.80	4.62	5.96	4.56
C	55.91	0.86	33.24	0.92	10.86	1.12	2.54	0.84

EXPERIMENTAL RESULTS

In this study, the data are presented as means by genetic horizons for each of three groups of profiles stratified according to acidity of the upper part of the solum. Group 1 includes three profiles in which the pH is above 6.8 throughout the solum; group 2, four profiles in which the A horizons are slightly acid, pH ranging mainly from 6.0 to 6.8; and group 3, three profiles in which the A horizons are medium or strongly acid, pH ranging from 5.0 to 6.0. Profiles of the three groups are shown diagrammatically as the Fenner series, the neutral extreme of the Honeoye series, and the acid extreme of the Honeoye series in figure 2 of the first paper of this series (2).

Table 1 gives the particle-size distribution as mean values by groups. All of the profiles except one were loam types. Two of the three profiles of group 1 approach fine sandy loams, and one, a silt loam; all profiles of group 2 approach silt loams; and all profiles of group 3 approach fine sandy loams. Texture is relatively uniform throughout the solums of group 1. Soils of groups 2 and 3 have strong clay maxima in the B horizons, the maximum being at a greater depth in the more acid soils.

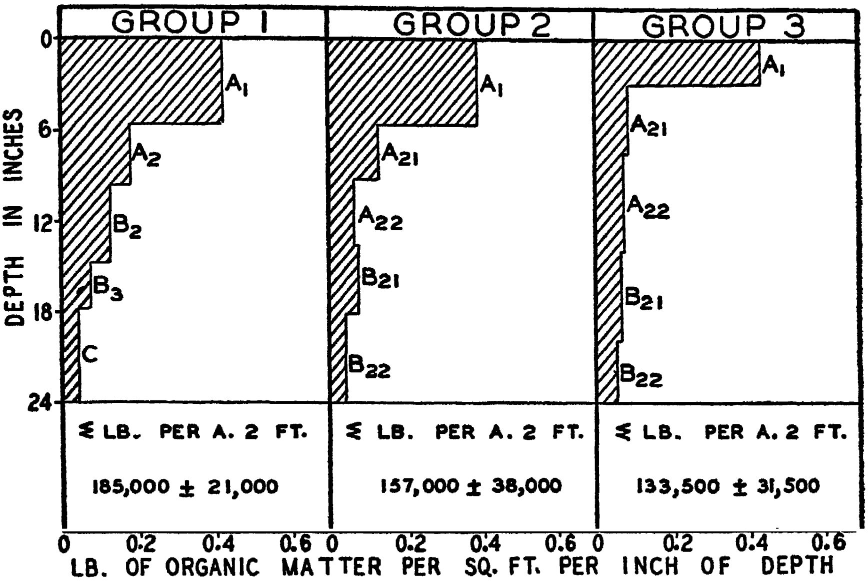

FIG. 1. MEAN ORGANIC MATTER CONTENT AND DISTRIBUTION WITH DEPTH IN PROFILES GROUPED ON THE BASIS OF ACIDITY OF THE A HORIZONS

TABLE 2

Mean and standard deviation of bulk density of genetic horizons of profiles grouped on the basis of acidity of the A horizons

HORIZON	GROUP 1		GROUP 2		GROUP 3	
	Mean	S D.	Mean	S D.	Mean	S.D.
A_1	1.01	0.15	1.08	0.06	1.03	0.07
A_{21}	—	—	1.52	0.13	1.31	0.10
A_{22}	1.44	0.08	1.57	0.13	1.71	0.17
B_{22}	1.62	0.04	1.55	0.07	1.67	0.17
B_3	1.58	0.04	1.60	0.17	1.61	0.14
C	1.80	0.11	1.65	0.13	1.70	0.06

The distribution of organic matter with depth in the upper 2 feet is shown in figure 1. Values are expressed as absolute amounts per unit volume based on the original determinations of bulk density and organic matter. Both the absolute amount and the depth of incorporation of organic matter decrease from the neutral to the acid soils. Variation among profiles of the same group is large, coefficients of variability ranging from 11 to 25 per cent of the means. Variability is of the same order of magnitude for individual horizons high in organic matter, but coefficients may be 50 per cent of the small means of horizons deep in the profile.

Bulk densities (table 2) are related to organic matter and clay contents of the horizons. Values increase sharply from the A_1 horizon, where organic matter concentration is highest, to the A_2. In the soils of group 1 there is a general increase with depth, but in the other two groups, both of which have pronounced textural profiles, there is a slight maximum in the A_{22} horizon, where both organic matter and clay are low. The values for the B horizons of these two groups are probably slightly too high because of errors inherent in the paraffined-clod method for soils with large aggregates.

TABLE 3

Mean and standard deviation of cation-exchange capacity of genetic horizons of profiles grouped on the basis of acidity of the A horizons

In milliequivalents per 100 gm.

HORIZON	GROUP 1		GROUP 2		GROUP 3	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
A_1	22.96	0.75	22.5	4.79	16.20	2.63
A_{21}	—	—	12.5	5.23	7.70	0.41
A_{22}	10.56	1.89	10.95	2.56	6.30	0.88
B_{21}	—	—	13.10	2.51		
B_{22}	10.50	2.36	14.30	2.71	8.90	1.28
B_3	9.26	1.00	12.60	1.48	7.90	0.77
C	4.13	0.79	6.40	1.84	4.79	0.24

The cation-exchange capacities (table 3) are functions of clay and organic-matter contents. The high exchange capacities of the A_1 horizons of all groups reflect their high concentrations of organic matter. In group 1, decreasing organic matter with depth more than compensates for the slight increase of clay in the B horizon and results in decreasing cation-exchange capacity with depth. Both of the other groups have minima in the A_2 and C horizons and maxima in the A_1 and B in conformity with the distribution of clay and organic matter. It will be noted that horizons of group 3 have consistently lower exchange capacities than do comparable horizons of the other two groups, which may also be explained by lower clay content, lower organic-matter levels, or a combination of the two. The trends of exchange capacity with depth, however, are remarkably similar for groups 2 and 3 and are characteristic of well-developed gray-brown podzolic soils.

Acidity of the A horizon is the basis on which profiles have been grouped, and table 4 shows the degree of segregation obtained and the variability in each group. The table also shows the general trends of pH with depth and indicates, indirectly, the relative losses of exchangeable bases from various horizons. Un-

TABLE 4

Mean and standard deviation of pH of genetic horizons of profiles grouped on the basis of acidity of the A horizons

HORIZON	Group I		Group II		Group III	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
A_1	6.98	0.14	6.12	0.33	5.72	0.02
A_{21}	—	—	6.22	0.28	5.17	0.27
A_{22}	7.32	0.24	6.15	0.33	5.82	0.51
B_{21}	—	—	6.45	0.35	5.70	0.10
B_{22}	7.52	0.19	6.56	0.78	6.52	0.57
B_3	7.75	0.01	7.07	0.52	—	—
C	8.35	0.20	8.11	0.22	8.33	0.06

TABLE 5

Mean chemical composition of genetic horizons of profiles grouped on the basis of acidity of the A horizons

In per cent

HORIZON	LOSS ON IGNITION	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	MnO
Group 1											
A_1	9.97	69.30	9.76	2.82	0.59	2.67	0.76	2.78	1.72	0.12	0.07
A_2	4.03	74.09	11.63	2.47	0.67	1.59	0.88	3.28	1.46	0.07	0.05
B_2	3.48	70.62	12.33	4.20	0.73	2.56	1.08	3.48	1.71	0.10	0.05
B_3	3.15	72.16	11.30	3.63	0.67	2.92	1.10	3.32	1.78	0.11	0.05
C	10.66	57.13	10.11	2.82	0.53	11.26	3.07	2.92	1.47	0.20	0.04
Group 2											
A_1	9.60	71.08	8.32	2.83	0.57	1.74	0.80	2.88	1.91	0.10	0.06
A_{21}	3.98	74.40	10.53	3.31	0.71	1.64	0.79	3.37	1.95	0.05	0.05
A_{22}	3.23	74.82	10.54	3.67	0.66	1.19	0.94	3.19	2.07	0.05	0.05
B_{21}	4.23	67.64	13.64	4.97	0.54	1.90	1.09	4.41	1.78	0.07	0.07
B_{22}	4.48	67.84	14.14	4.04	0.47	2.30	1.19	3.71	1.92	0.05	0.06
B_3	4.62	67.97	14.00	3.71	0.56	2.02	1.87	3.14	1.86	0.07	0.05
C	9.99	60.43	10.00	3.66	0.40	8.79	2.18	3.23	1.55	0.11	0.05
Group 3											
A_1	9.76	70.84	9.54	2.74	0.60	1.66	0.48	2.62	1.70	0.15	0.04
A_{21}	3.80	78.96	7.13	3.04	0.67	1.72	0.52	2.67	1.81	0.05	0.03
A_{22}	2.46	78.41	8.30	2.99	0.69	2.02	0.82	2.86	2.06	0.05	0.03
B_{21}	2.71	72.77	12.40	3.41	0.66	1.89	1.01	3.06	1.99	0.05	0.05
B_{22}	3.01	69.48	13.80	4.24	0.70	2.22	0.99	3.46	1.86	0.09	0.04
B_3	5.06	68.98	11.78	2.94	0.66	4.45	1.79	3.30	1.46	0.16	0.05
C	8.47	59.72	10.26	2.88	0.59	10.81	3.37	2.69	1.44	0.13	0.04

published data from other studies show that soils of this region are approximately 30 per cent base-saturated at pH 5.0; 55 per cent, at pH 5.5; and 80 per cent, at pH 6.0. It will be noted, therefore, that although carbonates have been lost to a much greater depth in group 2 than in group 1, exchangeable bases are high throughout the solums of both groups 1 and 2 relative to group 3.

Mean values from total chemical analyses are given in table 5 by genetic horizons for each of the three groups. In general, these data are characteristic of gray-brown podzolic soils, but the normal trends with depth are least striking for group 1 and are most strongly expressed in group 3. Loss on ignition reflects the concentration of organic matter in the A_1 horizons of all groups, the concentration of clays in the B horizons of groups 2 and 3, and the high carbonate content of C horizons of all groups. Silica is at a maximum in the A_2 horizons of all groups, but the most striking difference between horizons within each group is the decrease from B to C as a consequence of the diluting effect of carbonates in the C. The greatest differential of silica within the solum is in the group 3.

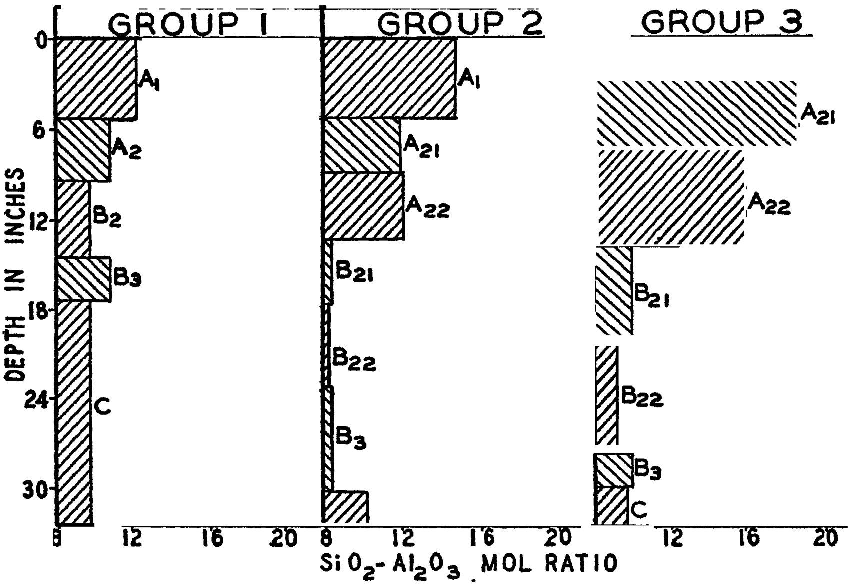

FIG. 2. SILICA-ALUMINA MOLECULAR RATIOS BASED ON MEAN CHEMICAL COMPOSITION OF GENETIC HORIZONS IN PROFILES GROUPED ON THE BASIS OF ACIDITY OF THE A HORIZONS

Alumina and iron distributions are the opposite of that for silica; the maxima in all groups are in the B horizon, and the minima are in the A. Absolute values reflect the clay distribution within profiles and among groups of profiles. The solums of all groups have lost large amounts of calcium and magnesium (mainly as carbonates) in comparison to the C horizons, and these losses strongly affect the relative values of all other constituents. The return of calcium to the surface by vegetation is apparent for group 1, is less evident for group 2, and is not apparent from the data for group 3. Except for this effect, both calcium and magnesium increase with depth. Potassium is at a minimum in the A_1 horizon and a maximum in the B in all groups, whereas sodium is at a minimum in the C of all groups. The highest phosphorus concentrations are in the A_1 hori-

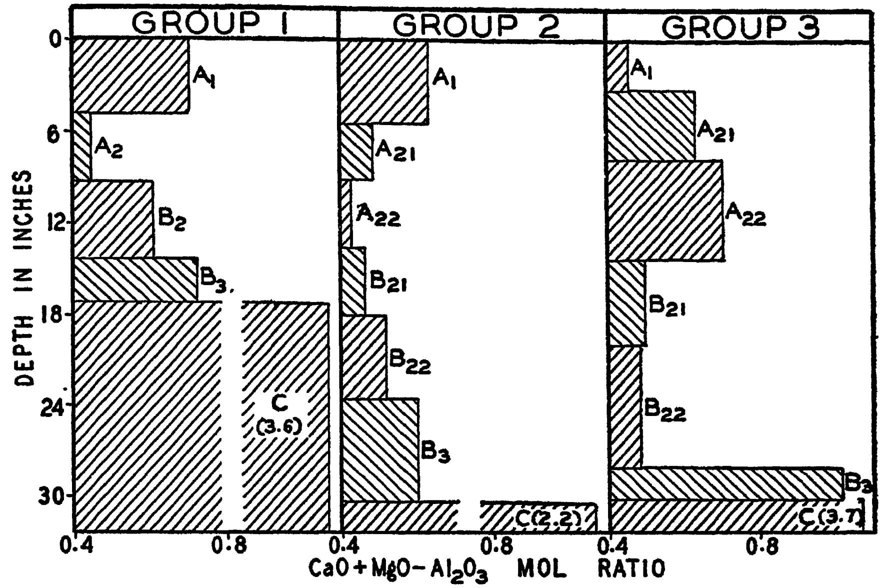

FIG. 3. MOLECULAR RATIOS OF THE SUM OF DIVALENT BASES TO ALUMINA, BASED ON MEAN CHEMICAL COMPOSITION OF GENETIC HORIZONS IN PROFILES GROUPED ON THE BASIS OF ACIDITY OF THE A HORIZONS

TABLE 6

Molecular ratios of genetic horizons in profiles grouped on the basis of acidity of the A horizons

HORIZON	CaO/Al_2O_3			MgO/Al_2O_3			$MgO + CaO/K_2O + Na_2O$		
	Group 1	Group 2	Group 3	Group 1	Group 2	Group 3	Group 1	Group 2	Group 3
A_1	0.50	0.38	0.32	0.20	0.25	0.13	1.17	0.83	0.75
A_{21}	—	0.29	0.44	—	0.19	0.19	—	0.74	0.77
A_{22}	0.25	0.21	0.45	0.19	0.21	0.25	0.86	0.66	0.89
B_{21}	—	0.25	0.28	—	0.21	0.21	—	0.82	0.92
B_{22}	0.38	0.30	0.29	0.22	0.21	0.19	1.13	1.00	0.96
B_3	0.47	0.26	0.69	0.25	0.34	0.39	1.24	1.30	2.12
C	2.07	1.62	1.91	1.50	0.56	1.74	6.49	3.57	7.16

	$K_2OAl_2O_3$			Na_2O/Al_2O_3			Fe_2O_3/Al_2O_3		
	Group 1	Group 2	Group 3	Group 1	Group 2	Group 3	Group 1	Group 2	Group 3
A_1	0.31	0.38	0.30	0.29	0.38	0.30	0.18	0.22	0.18
A_{21}	—	0.35	0.41	—	0.20	0.41	—	0.20	0.27
A_{22}	0.31	0.33	0.38	0.20	0.32	0.41	0.14	0.22	0.23
B_{21}	—	0.35	0.27	—	0.21	0.26	—	0.23	0.18
B_{22}	0.31	0.28	0.27	0.22	0.23	0.23	0.22	0.18	0.19
B_3	0.32	0.24	0.31	0.26	0.22	0.20	0.20	0.17	0.16
C	0.32	0.35	0.28	0.23	0.26	0.23	0.18	0.24	0.18

zons in association with high organic-matter levels and in the relatively slightly weathered C horizons.

Relative concentration of silica with respect to alumina is shown in figure 2. With increasing acidity from group 1 to group 3, alumina decreases greatly with respect to silica in the A horizons. The iron-alumina molecular ratios in table 6 indicate some concentration of iron with respect to alumina with increasing acidity.

Molecular ratios of the sum of divalent bases to alumina are shown graphically in figure 3. The loss of these bases relative to loss of alumina in the solums of all groups is very striking when C horizons are compared with any horizon of the solum. The return of bases by vegetation to the A_1 horizon noted previously is reflected in the graphs of groups 1 and 2, but in the acid soils of group 3, this process has not offset losses of bases relative to aluminia.

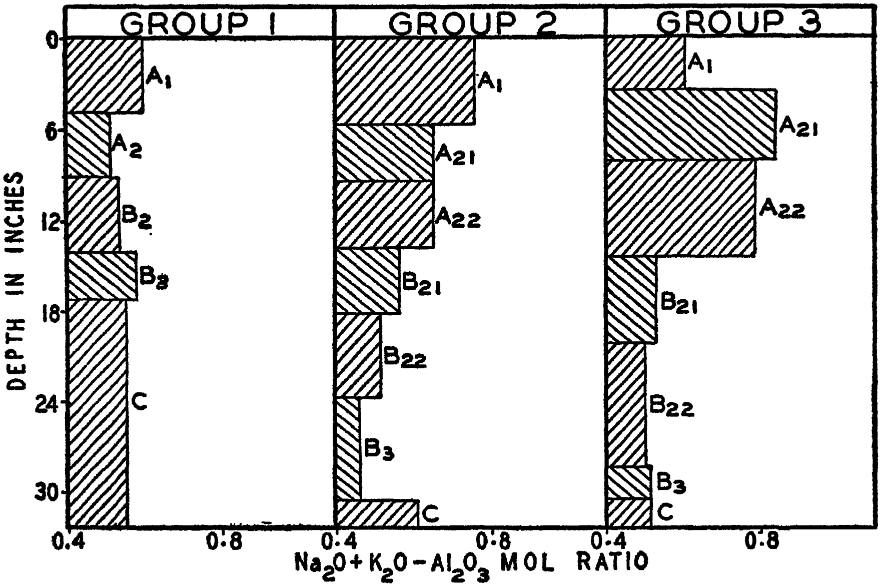

FIG. 4. MOLECULAR RATIOS OF THE SUM OF MONOVALENT BASES TO ALUMINA, BASED ON MEAN CHEMICAL COMPOSITION OF GENETIC HORIZONS OF PROFILES GROUPED ON THE BASIS OF ACIDITY OF THE A HORIZONS

Molecular ratios of monovalent bases to alumina are shown in figure 4. The ratios are remarkably uniform throughout the solums of the soils of group 1. Losses of alumina relative to monovalent bases in the slightly acid soils of group 2 have been large in the upper, most acid horizons but decrease with depth and increasing pH within the profile. This relationship to pH is even more pronounced in the medium to strongly acid profiles of group 3.

DISCUSSION

It is self-evident that each of the profiles used in this study must have evolved by a succession of changes from the unaltered glacial till of Pleistocene time to the soil profile sampled. Following Kubiena's reasoning (11), one would expect a succession of stages of soil development to have evolved with time. At any given stage, many physical, chemical, and biological processes must have operated concurrently, some at such slow rates as to have been negligible and others at such rapid rates as to have dominated the net effects on soil formation. As long as the *relative* rates of contributing processes remained unchanged, one would expect soil development to have been restricted to increasing degree of expression of a given combination of soil properties. Development in these terms, however, implies changes of the soil that would ultimately have affected *relative* rates of processes, and this would be expected to have led to development of new sets of soil characteristics. Of all of the changes known to have occurred, none would have exercised greater control over rates of many contributing processes than depletion of bases and consequent development of acidity.

The base status of the profiles studied has decreased with time but to different degrees among the three groups. There is no evidence of major geologic unconformity within any of the profiles studied, and it may be assumed that the glacial till at all sites was originally strongly calcareous throughout. Loss of both carbonates and exchangeable bases would have occurred as a function of factors that would have affected rates of leaching and return of bases in vegetation. Of these, differences of permeability would be the most likely to have caused the observed differences in base status, but whatever the cause may have been, the fact remains that the three groups have reached different stages of base depletion in approximately the same time.

There is no way to determine the course followed by depletion of bases in the profiles studied, but it would be expected to have approximated the trends of increasing acidity and depth to carbonates (depth to the C horizon) from group 1 to group 3 in table 4. One would expect maximum losses to have occurred in the upper horizons but to have been offset to some extent in the A_1 by return of bases by vegetation. Depth to carbonates should have increased, and pH of a given horizon should have decreased with time, the compensating return of bases becoming more apparent in pH profiles though smaller in absolute amount as acidity increased. On this basis, it may be assumed that the base status of each of the three groups approximates that of a former stage in the depletion of bases of soils that are now more acid, without denying the possibility that the base status of each profile studied may be an equilibrium condition under the special circumstances of its external and internal environment. *Absolute* rates of processes may have been limited by local environmental factors to such a degree that at lease quasi-equilibrium with geomorphic processes would be established at a stage through which dominant soils of the region would normally have passed.

If it may be granted that decreasing base status from group 1 to group 3 approximates the expected course of base depletion with time, it can be shown that the observed differences of amount of organic matter, amount and distribution of clay, and chemical composition of genetic horizons would also approximate the general course of expected changes with time, although the absolute magnitudes of the properties involved might vary in different absolute time scales.

Organic matter

Organic-matter levels (fig. 1) are correlated with base status in these soils. Dawson (4), using the concepts of Jenny (10), Nikiforoff (14), and Salter and Green (19), has developed quantitative relationships for organic-matter balance around a basic assumption that soil humus in a given environment is a function of the balance between additions and losses of nitrogen. In line with Dawson's reasoning, organic matter would be expected to decrease with increasing acidity as a consequence of decreasing nitrogen fixation and probable decreasing effectiveness of vegetation in conserving the nitrogen present. Increasing acidity should reduce nitrogen fixation directly, and possibly indirectly also by reducing legumes in the vegetation. Depletion of bases might also cause a decrease of nitrogen uptake by vegetation, either by changes in composition of the stand or reduction of growth rates. The net effect should be to decrease the level of nitrogen balance and organic-matter content as functions of decreasing base status with time. The observed differences of organic matter among soil groups are small but consistent in trend and are commensurate with the relatively small decrease of bases among these profiles, which represent only a segment of the sequence described in the first paper of this series (2). Similar correlation between biological activity, organic-matter content, and base status has been reported by Kubiena (11) for comparable soils in Europe.

Clay distribution

The position in the profile and degree of expression of the textural B horizon (table 1) are apparently related to loss of bases and development of acidity as a function of time. It will be noted in table 1 that clays decrease sharply with depth at the point below which carbonates occur. Part of the difference between B and C horizons can be attributed to dilution by carbonates, as Mickelson (13) and Mick (12) have demonstrated, but recalculation of the data on a carbonate-free basis still leaves a differential clay content of the order of 2 to 1. This characteristic, therefore, appears to represent a real differential accumulation of clays within the solum, and the depth of that accumulation appears to be a function of increasing depth to carbonates. It will also be noted in table 1 that a clay minimum occurs in the A horizon and that its magnitude and depth in the profile appear to be functions of increasing acidity with time. Theoretical considerations would cause one to expect these relationships although the development of the textural B horizon in gray-brown podzolic soils may be the net result of several processes.

Theoretically at time zero, the clay-mineral distribution should be uniform as to both species and amount throughout the upper part of the till profile. As soil formation progresses, probably new kinds of clay minerals or new amounts of the original kinds would be formed, and this assumption is supported by preliminary evidence of alteration of micas to a vermiculite, which could be an intermediate stage in clay formation. In accord with the principles of polyfunctional weathering presented by Jackson *et al.* (9), clay destruction should be proceeding concurrently with clay formation, and the net gain or loss of clay in the solum as a whole should be determined by the balance between these two processes as a function of time. The dominant species present should ultimately be those most resistant to weathering under the internal environment of each horizon.

One would expect clays to be formed more rapidly in the solum than in the C horizon on the basis of Stevens' conclusion (20) that carbonates inhibit weathering of silicates, which would be the parent materials of clays. Consequently, the zone of most rapid clay formation should follow the calcareous C horizon downward as a function of time. Jackson *et al.* (9) point out that the effects of depth as such on weathering intensity are small within depth limits like those studied here.

The clay mineral species that accumulate during the early stages of base depletion should be those most stable under conditions of neutrality, as in profiles of group 1 or in the B horizons of all groups. As acidity develops with time, changes in the *relative* rates of clay formation and destruction would be expected because both acidity and specific surface are involved. Jackson *et al.* (9) found silicate clays to be more stable than minerals that are their parent materials, if they are of comparable particle size, but these authors also point out that both increasing specific surface and increasing acidity accelerate weathering. As the minerals from which clays are derived are concentrated mainly in the coarser size fractions, it is reasonable to expect that acceleration of weathering by increasing acidity would affect the rate of silicate clay destruction more than it would the rate of clay formation for those species that would accumulate under a neutral environment. Possibly, the absolute rates of destruction of some species of silicate clays could surpass their rates of formation from "less resistant" but coarser minerals as acidity increases with time. Thus, the high clay contents of neutral horizons might be attributed to more rapid formation than destruction of silicate clays, and the low clay contents of acid horizons, to more rapid destruction than formation. This could account, in part, for the observed increase in magnitude and depth of the clay minimum in the upper part of the profile from group 1 to group 3 in table 1.

Acceleration of clay weathering with increasing acidity would not be likely to account for all of the differences observed, especially between groups 1 and 2, both of which have relatively high pH values throughout the solum. Clay migration from the A to the B horizon appears to be an important contributing process even in soils that are only slightly acid. Petrographic examination of thin sections of comparable soils (6) has provided positive evidence of the migration of clay from the A to the B horizon. Removal of clay from the A appears to be related to the distance from voids as a means of exit either of clay particles or of soluble end-products of weathering. Some zones of residual clay are evident where no means of exit are present, even in the A_2 horizon. In the B horizons, masses of clay are conspicuous in layers along the voids in addition to disseminated masses which either could have been inherited or could have formed in place. Petrographic evidence of orientation of these clays parallel to the pore walls is convincing evidence of secondary enrichment from percolating waters.

Acidity should be an important factor governing peptization of clays in the A and isoelectric precipitation in the B; therefore, the thickness of the zone of eluviation and the depth of the clay accumulation in the solum should be related to loss of bases as a function of time and permeability of the profile.

Chemical composition

There are consistent trends of chemical composition among groups. Within the solums, silica, sodium, potassium, calcium, and iron increase relative to aluminum with increasing acidity among comparable horizons of the three groups and, except for calcium, among horizons of the same group (figures 2, 3 and 4 and table 6).

By a process of elimination, it can be shown that the major trends noted above reflect mainly the observed decrease of clays with increasing acidity.

1. After removal of carbonates, the major classes of minerals in the parent materials of these soils would be quartz, feldspars, micas, and silicate clays with smaller proportions of amphiboles, pyroxenes, and possibly oxides of iron and aluminum.

2. The increase of SiO_2/Al_2O_3 ratios with increasing acidity in figure 2 indicates accelerated loss of some aluminum-bearing mineral relative to quartz. A high degree of stability of quartz in the silt and sand fractions would conform with the Goldich stability series (7). Jackson *et al.* (9) point out that marked insolubility of silica occurs at pH values far below those in these soils; therefore, differential loss of alumina and accumulation of silica from aluminosilicates would not be expected. The small secondary maximum at high pH in the B_3 horizon may be the result of pyrophyllite formation as suggested by Mickelson (13).

3. The trends of Na_2O/Al_2O_3 and K_2O/Al_2O_3 mol ratios with increasing acidity in table 6 suggest accelerated loss of some aluminosilicate relative to sodic and potash feldspars as acidity increases. Ratios of monovalent bases to alumina, as calculated from data by Pettijohn (17), Dana (3), and Dennison *et al.* (5), approximate 1.0 for orthoclase, microcline, and albite; 0.14 to 0.56 for biotite; 0.27 to 0.35 for muscovite; and 0.35 for illite. The ratios of figure 4 approach the theoretical maximum of the feldspars in the most acid horizons of group 3. This would indicate that the concentration of "high-ratio" minerals has increased relative to the "low-ratio" minerals in the more acid horizons of group 3. In the neutral horizons of group 1 the value is near 0.4, which indicates no relative concentration of "high-ratio" minerals. The ratios in group 2 are intermediate, suggesting an intermediate concentration of "high-ratio" minerals. As differential loss of end products of weathering of feldspars would be expected to result in trends opposite to those observed, the trends with increasing acidity apparently result from differential acceleration of loss of "low-ratio" minerals like micas, clays, or those that contain no monovalent bases.

4. By similar reasoning, the CaO/Al_2O_3 ratios in table 6 and $CaO+MgO/Al_2O_3$ ratios in figure 3 suggest that increasing acidity increases the loss of micas, vermiculites, or silicate clays more than the loss of minerals that carry higher proportions of calcium. The principal sources of divalent bases in the solum should be plagioclase feldspars, pyroxenes, amphiboles, micas, epidote, vermiculites, and silicate clays. Of these, all except feldspars and epidote would contribute magnesium or both megnesium and calcium. It will be noted in table 6 that MgO/Al_2O_3 ratios show no consistent trends with increasing acidity, indicating that the acceleration of losses of alumina noted above must be matched by acceleration of losses of magnesium as acidity increases. Plagioclase feldspars, or epidote or both appear to be concentrated as acidity increases by acceleration of the loss of one or more of the minerals that contribute mainly aluminum and magnesium to the ratios. The pyroxenes and amphiboles should contribute little aluminum but contain both magnesium and iron.

5. It will be noted in table 6 that Fe_2O_3/Al_2O_3 ratios suggest greater loss of alumina than of iron with increasing acidity. Data of Frei and Cline (6) show that iron oxide films on sand particles increase with increasing acidity, which suggests increased rates of weathering of ferromagnesian minerals, the iron remaining in the profile. This would conform with the weathering sequence postulated by Goldich (7). Humbert and Marshall (8) report synthesis of epidote presumably from weathering products of plagioclase feldspars, pyroxenes, and amphiboles, which would lead to conservation of calcium with respect to magnesium as noted here and also would permit an increase of Fe_2O_3/Al_2O_3 ratios if the iron were not lost.

All of these criteria point to micas, vermiculities, or clay minerals as the principal sources of differential loss of alumina with increasing acidity, with the possibility of differential loss of oxides of aluminum in the more acid horizons. Preliminary petrographic studies show a high degree of alteration of micas to vermiculite in profiles of group 2, and this could well be the first stage in the formation of silicate clays. Although desilication would be the major process involved in alteration of these silicates under the neutral or alkaline conditions that existed originally, iron and aluminum oxides might be released by weathering of these or other minerals in some quantities. Increasing acidity would accelerate their loss, which would contribute to the trends of chemical composition observed. The major part of these trends, however, appears to be a reflection of accelerated loss of silicate clays by weathering or translocation or both.

SUMMARY

Particle-size distribution, bulk density, organic matter, cation-exchange capacity, pH, and total chemical composition were determined for genetic horizons of each of 10 profiles ranging from neutral intergrades between brown forest and gray-brown podzolic soils to strongly acid gray-brown podzolic soils. The profiles were grouped on the basis of acidity of the A horizons to give three groups approximating three successive stages in the depletion of bases in soils on calcareous parent material. With decreasing base status in the A horizons, (*a*) organic matter decreases, (*b*) depth of solum increases, (*c*) thickness of the A_2 horizon increases, (*d*) magnitude of the clay maximum in the B horizon increases, and (*e*) aluminum decreases with respect to silica, sodium, potassium, calcium, and iron among comparable subdivisions of the A horizon. Aluminum and magnesium remain at near-constant proportions. The decrease of aluminum with respect to other constituents is attributed to an increase in the rates of loss of silicate clays with respect to rates of weathering of minerals in coarser size fractions as acidity increases. It is suggested that the observed trends among groups of profiles are functions of base depletion with time and that each of the groups of profiles approximates a stage in the development of more acid soils, although any of the groups sampled may be an equilibrium product of its particular environment.

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BOOKS

American Potato Yearbook. Edited by JOHN C. CAMPBELL. Agricultural Experiment Station, New Brunswick, New Jersey, 1950. Pp. 76. Price, paperbound, $2.

The purpose of this yearbook is to record in one volume all the agencies and associations that are concerned with the development of the potato industry. In addition, the booklet contains a large number of statistical data on potato acreage, production, and prices and presents information on certified seed and quality of produce. It also gives the rules and regulations affecting shipments of seed potatoes and price support schedules. Recent books on potatoes are reviewed and other matters of interest to the industry are reported on.

Annual Review of Plant Physiology. Edited by D. I. ARNON. Annual Reviews, Inc., Stanford, California. Pp. 364. Price $6.

This is volume 1 of what is expected to be a series of annual reviews of advances in plant physiology. It contains 15 papers on mineral nutrition, carbon dioxide fixation, light relationships, tropisms, organic acids, sugars, growth-regulators, herbicides, cell-wall growth, biochemistry of fruits, respiration, nitrogenous constituents, water relations, soil moisture, and soil chemistry, all in relation to plants. The authors are outstanding specialists in these respective fields of research. The reviews are largely limited to work conducted during the last 2 to 5 years. Attached to each review is a long list of references. The publications of some 1,800 workers in plant physiology are covered. The subjects to be reviewed in volume 2, with their authors, are also shown. One of the most interesting of the reviews in volume 1 is that of Thimann and Bonner on organic acid metabolism, which contains a very complete statement on the occurrence and distribution of such acids in plants. The general excellence of all the reviews is such that every worker in soil-plant science will want a copy available for ready reference.

The Biogeochemistry of Vertebrate Excretion. By GEORGE EVELYN HUTCHINSON. American Museum of Natural History, New York, 1950. Pp. 554, figs. 103, plates 16. Price, paperbound, $10.

This is bulletin 96 of the Survey of Contemporary Knowledge of Biochemistry. It has to do with the deposition and nature of bird and bat guanos. The primary point of interest lies in the total amounts of nitrogen and phosphorus contained in these materials. The extent of the old and new deposits is recorded, as are also the factors which determined their rate of deposition, the chemical composition of the nitrogenous guanos, the nature of the phosphatic guanos, and the locations of the several deposits. Consideration is also given to the cave guanos and to the geochemistry of guano mineral. A tremendous amount of study and work has gone into the preparation of this volume. The material contained in it is of great historical as well as current interest. Among the unique points developed are those dealing with the formation of oxalic acid from uric acid, the high copper content of some of the bat guanos, and the statement that only a small percentage of the phosphorus that is lost from the land to the sea is returned in the guano. A bibliography of references to the work of some 700 authors is appended. For those who are interested in guanos, this is a very important volume.

Centennial. American Association for the Advancement of Science. Washington, D. C., 1950. Pp. 313. Price $5.

The American Association for the Advancement of Science celebrated its first 100 years of existence by holding a meeting at Washington, D. C., September 13–17, 1948, and this book contains the 42 addresses of the scientists who were invited to speak on that occasion. The papers cover a wide range of subjects on science in relation to society, educational potentials, human individuality, nutrition, housing, health problems, sources of energy, upper atmosphere, natural resources, genes and cytoplasm, high polymers, interactions of matter and radiation, and waves and rhythms. Soil-plant scientists will be especially interested in "Nutrition and Climatic Pattern of Soil Development," by William A. Albrecht; "Seven Decades of Nutrition Research," by A. C. Elvehjem; "Science and Control of Human Population," by Warren S. Thompson; "Solar Energy," by Farrington Daniels; "Living on the Biosphere," by G. E. Hutchinson; "Plants and Vegetation as Exhaustible Resources," by Stanley A. Cain; "Exploitation of Mineral Resources," by T. S. Lovering; and "Genes as Determiners of Cellular Biochemistry," by David M. Bonner. The book contains the substance of a liberal education in science and should enjoy a very wide reading.

Forever the Land. Edited by RUSSELL LORD. Harper and Brothers, New York, 1950. Pp. 394. Price $5.

Russell Lord has the happy faculty of being able to draw to himself those who have an abiding faith in the good earth as a rejuvenating force for man himself, as well as for the plants and animals that grow on the farm. Many of these country-minded folks have tried to put their thoughts into words, and Lord has selected the most attractive of these bits of prose and poetry for this anthology. Kate Lord, his wife, has added an equally important touch in her line drawings of farm scenes, by which she somehow conveys to the reader some of the peace and serenity that obtain. The book is an outgrowth of the Friends of the Land movement, and many of the selections were originally published in that society's journal, "The Land." All country-minded farm and city folks will find this book very attractive reading. It is one of the type that can be kept at hand to advantage for pick-up reading as time permits.

Geomorphology. By NORMAN E. A. HINDS. Prentice Hall, Inc., New York, 1943. Price $8.

The subtitle on this very attractive book is "The evolution of a landscape." The author has developed his subject largely on the pictorial basis. Some 750 illustrations, largely reproductions of photographs but supplemented by a considerable number of excellent drawings, aid the reader in understanding the text. It is not clear for whom the book is written, but one gets the impression that it is designed primarily for the more inquiring types of persons who vacation about the country without having any very definite concepts of the geological happenings of the past. It could be used to advantage in a cultural course in an arts college. A bibliography of more than 700 references is appended. The book has permanent value.

Hydrology. Second Edition. By Daniel W. Mead. McGraw-Hill Book Company, Inc., New York, 1950. Pp. 728, figs. 397. Price $7.50.

This second edition was revised and enlarged by Mead and Hunt, Inc., Consulting Engineers. The work was done largely by Henry J. Hunt, who has long been associated with Professor Mead. A number of enlargements and improvements in the discussion have been effected, with special reference to measurements of evaporation, means of producing artificial rainfall, methods of weighing precipitation records, application of the theory of probability to drought and flood frequencies, and the increasing demands for water by cities and industries. The book contains a large amount of very important and interesting information on winds, storms, hydrography, evaporation, precipitation, great rainfalls, droughts, geological agencies, ground waters, stream flow, runoff, and floods. The last chapter is concerned with the applications of hydrology. A list of important references is appended to each chapter. The large number and excellence of the illustrations add greatly to the readability and value of the volume. Most of those who are concerned with soil and water conservation would benefit greatly by having a copy for study and reference.

Iodine and Plant Life. Chilean Iodine Educational Bureau, London, 1950. Pp. 114.

This is a paper-bound annotated bibliography of the literature on iodine covering the period between 1813 and 1949, with a 24-page review of the literature. It reports the iodine content of seaweeds and land plants, the effect of iodine on the growth and well-being of plants, animals, and microorganisms, and the use of the element for plant-protection purposes, including seed disinfection, weed-killing, and as an insecticide. A total of 794 papers are reviewed. The Bureau has made a highly important contribution to scientific literature by compiling this material.

The Nutritional Improvement of Life. By Henry C. Sherman. Columbia University Press, New York, 1950. Pp. 270. Price $3.75.

"No longer need it be so generally true, as once it appeared to be, that life after 70 is but burden and sorrow." That sentence gives an indication of the concern of the author in writing this book. Included among the many factors mentioned as important for better health are: lowering consumption of protein, increasing the calcium content of the diet, including adequate amounts of vitamin A, giving more consideration to beans and nuts, "marrying health and agriculture," and recognizing that heredity may be "enhanced, dwarfed, warped, or mutilated in its expression," depending on nutritional factors. The author agrees with George R. Minot who said: "Man's future will depend very largely upon what he decides to eat." The final chapter deals with the subject of better nutritional status for more people. The appendix includes the 1946 world food survey, records of actual food consumption, and a selected bibliography of about 400 references. The book should find a place on the shelves of all those who are concerned with the production and processing of food plants.

Plant Viruses and Virus Diseases, Third Edition. By F. C. Bawden. The Chronica Botanica Co., Waltham, Massachusetts, and Stechert-Hafner, Inc., New York, 1950. Pp. 335, figs. 59. Price $6.

One chapter and many new illustrations were added to the third edition, and much of the text was rewritten. This was necessitated by the rapid advances that have been made in this field of research. The introductory chapter defines the nature of viruses. The succeeding chapters deal with external and internal symptoms, methods of transmission, relations between viruses and vectors, mutations, serological reactions, methods of assaying, purification, properties, inactivation, toxonomy, relation to the host, control measures, and speculations as to origin. A long list of references is appended to each chapter, the work of some 500 authors being reviewed. The illustrations are excellent and of extraordinary interest to the soil-plant scientist. The book is the work of a skillful writer who has presented the subject in a very attractive manner. The last chapter is of special importance in that it deals with two questions: Are viruses living things? and How do viruses originate? The book fills a highly important need, and every plant specialist will want a copy close at hand for ready reference.

Pocket Encyclopedia of Atomic Energy. By Frank Gaynor. Philosophical Library, Inc., New York, 1950. Pp. 204. Price $7.50.

The purpose of this book is to present definitions and explanations of the many terms that are being employed in discussions of atomic energy. Individual entries for each element cover properties of stable forms and radioisotopes. Important research laboratories and installations are shown. Short biographical sketches are given of the most prominent personages in this field of science. German equivalents are given for some of the terms as a convenience to those who are studying German literature on this subject. Among the more than 2,000 entries are 34 tables, charts, and illustrations. The book is especially useful for the beginning student in this science but has value also to those who are already working in this field of research.

Rainfall and Runoff. By Edgar E. Foster. The Macmillan Company, New York, 1949. Pp. 487, figs. 179. Price $9.

The author of this book presents an excellent picture of the science of hydrology as related to rainfall and runoff, with statistical analyses of the available data. He begins with a consideration of the principles involved and then proceeds with a discussion of precipitation, air masses, storms, evaporation, runoff, floods, ground water, and use of hydrological data. A list of 200 references is appended. The acts of Nature are accepted and analyzed without reference to any possible controls that might be applied by man. But the author provides the data that are necessary to be assembled before the scientist who is concerned with soil and water conservation can begin his research program. The book is of special value for reference for those who have to do with the control of rainfall and the use of water for agricultural and other purposes.

The Recovery of Culture. By HENRY BAILEY STEVENS. Harper and Brothers New York, 1950. Pp. 247, figs. 6. Price $3.

The author of this book follows, with highly interesting details, the development of the primate family during the last 60 million years and then carefully analyzes some important happenings during the age of man. He comes to the conclusion that somewhere along the path of life mankind took the wrong turn and that, as a result, the whole world is in turmoil. That wrong turn had to do with the change from vegetarianism to flesh-eating. Wars, soil erosion, and impoverished and starving peoples are the result. It is seldom that a reader finds himself confronted with such a radical departure from the common thought. The book merits wide reading by thoughtful men.

Science and Foreign Relations. By LLOYD V. BERKNER. Department of State Publication 3860, 1950. Pp. 170.

This is a report of a special consultant to the Secretary of State, looking toward the establishment of a group of scientific advisors who would gather and disseminate nonsecret research information. It recommends that American scientists be sent to all foreign gatherings of scientists and that foreign scientists be encouraged to attend such meetings in this country. The net effect of this proposal would be to keep the channels open for the ready movement of scientists and their concepts. The consulting scientists presumably would play important parts in determining the policies of the Department of State. They would be attachés with full diplomatic status.

Soil Fertility. By L. M. THOMPSON. William C. Brown Company, Dubuque, Iowa, 1949. Pp. 136, figs. 46. Price $1.25.

This is a loose-leaf, spiral-bound set of notes employed by the author to save the student's time in class. Its several chapters deal with factors affecting plant growth, clay minerals, soil reaction, liming practices, nitrogen, phosphorus, potassium, fertilizer practice, manures, and plant composition. The presentation is built around the soil and agricultural requirements of Iowa, but much of the material is generally applicable. The loose-leaf system permits of continuous revision and that, no doubt, is the author's intention. The material is well chosen and is illustrated by graphs. A list of references is appended to each chapter. The appendix contains 9 tables of data for reference in calculations related to the several nutrients in soils, plants, and fertilizers.

THE EDITORS.

SOIL SCIENCE

VOLUME 70 *November 1950* NUMBER 5

FORMATION OF QUAGMIRES (PHODAS) IN SOILS OF THE NIZAMSAGAR PROJECT AREA, HYDERABAD STATE, INDIA

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Received for publication April 29, 1949[1]

Since 1943, the Nizamsagar Development Board of the Government of Hyderabad Deccan has sponsored quagmire research and reclamation in the Nizamsagar area, the location, topography, natural vegetation, climate, and soils of which were previously outlined.[2]

The present paper describes the formation and morphological features of quagmires in this area and discusses remedial measures.

SALINIZATION OF SOILS

The leaching process predominates in the soils of the Nizamsagar area, as the annual precipitation is heavy, varying from 30 to 50 inches. Readily soluble salts such as the bicarbonates, chlorides, sulfates, and carbonates of sodium, potassium, calcium, and magnesium are transported from higher to lower levels and tend to accumulate in pocket-like areas, depressions, midslopes, and valley basins. Hidden saline soils[3] are thus first formed. The ground water in these soils has a high salt concentration. The chemical composition of such ground waters from widely scattered areas is given in table 1.

With the progress of salinization, highly alkaline patches of soil are formed, and the native vegetation, unable to tolerate the high concentration of salts in the soil, finally disappears. The chemical composition of the surface salt scrapings from different saline patches of soil is given in table 2.

FORMATION OF QUAGMIRES

In the alkaline patches with bad drainage and damp subsoils, small, circular, fluffy saline spots are observed. Characteristic salt- and water-loving vegetation springs up in and around these spots, which develop at different rates into quagmires, locally known as "phodas." Salts tend to accumulate in the subsoil overlying the impervious disintegrating parent material. As the bulk of these are sodium salts, much sodium enters the clay complex. The subsoil absorbs 64 to 381 per cent water, on an oven-dry basis, and assumes a fluid state due to dispersion of the sodium clay. The absorption of an enormous quantity of water by the clay causes swelling, which exerts great pressure on the surface soil. As a result, the surface soil is lifted into flat-topped cone-shaped knolls, which finally burst open. Much slimy fluid is ejected from the center of these quagmires.

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MORPHOLOGY OF QUAGMIRES

Quagmires have been encountered which range from a few inches to 3 feet in height above ground level and from 3 to 25 feet in diameter. In the red sandy loams, the depth varies from 3 to 6 feet, which corresponds with the depth at which the parent rock material lies. In the black sandy clays and clays, the depth is very great. Quagmires in the red and black soils are shown in figures 1 and 2.

TABLE 1

Chemical composition of ground waters in hidden saline soils

VILLAGE AND SURVEY NO.	pH	CO_3	HCO_3	Cl	SO_4	Ca	Mg	Na	K
		ppm.	*ppm*	*ppm.*	*ppm*	*ppm*	*ppm.*	*ppm*	*ppm*
Jakora, 201	8.3	18	470	27	38	216	15	146	54
Kothapally, 340	8.4	26	185	14	0	11	49	46	3
Rakoor, 162		39	225	4359	1570	82	502	2372	12
Rudrur, 258	8.9	48	403	39	46	88	34	112	44

TABLE 2

Chemical composition of surface salt scrapings from soils

VILLAGE AND SURVEY NO.	CO_3	HCO_3	Cl	SO_4	Ca	Mg	Na	HUMUS
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
olloor, 127	tr.	0.63	7.80	28.19	0	1.31	27.29	4.66
akli, 21	0	0.29	2.12	31.49	0	0.87	28.89	3.49
albhapur, 96	0	0.42	9.92	25.72	8.27	1.57	16.70	4.66
albhapur, 63	tr.	0.52	3.54	30.83	0.77	0.96	28.83	4.43

Ejection of fluid is illustrated in figure 3. Figure 4 presents a bird's eye view of a patch of quaggy clay soil.

Figure 5 illustrates the surface of a quagmire during summer. The central portion (A) is watery. The yellowish or whitish fluid starts solidifying from the sides of the quagmire as summer progresses. Salts deposited on the surface form a white incrustation—solonchak (B). Black patches of solonetz incrustations (C), which result from dissolution of humus by sodium carbonate, are commonly observed. The ejected fluid, on drying, cracks into multisided, highly baked, very hard clods (D).

The characteristic salt- and water-loving weed and grass vegetation of the quagmire is illustrated in figure 6.

The fluid in the quagmire contains a free admixture of ferruginous concretions, white lime concretions, black manganese nodules, and yellowish angular quartz

Fig. 1

Fig. 2

Fig. 1. Quagmire in Red Soil
Fig. 2 Quagmire in Black Soil

Fig. 4

Fig. 4

Fig. 3. Ejection of Fluid from Quagmire
Fig. 4. Quagmires on Clay Land

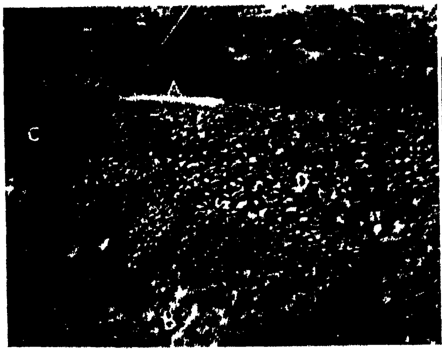

Fig. 5

Fig. 6

Fig. 5 Surface of Quagmire During Summer
Fig. 6. Vegetation of Quagmire

pieces, which are commonly encountered in a majority of the soils of the tract. A vertical section of a dried quagmire exhibits a structureless, highly sticky clay mass.

Fluid samples from quagmires occurring in widely scattered areas were analyzed for their water-soluble salts. The results are recorded in table 3. The fluid is highly alkaline, with pH values ranging from 8.3 to 8.5. The bulk of the soluble salts are those of sodium, which is the predominant cation. The anions are carbonates and chlorides. The carbonates are present mostly as bicarbonates and partly as normal carbonates. Sulfates are entirely absent. Alkali carbonate is predominant, NaCl is negligible, other electrolytes like Na_2SO_4, and flocculating cations like Ca are totally absent.

TABLE 3

Soluble-salt content of fluid from quagmires*

VILLAGE AND NO.	pH	CO_3	HCO_3	Cl	Mg	Na	K	TOTAL
		ppm.	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*
Akbarnagar, a	8.30	122.4	1244	71	54	595	0	2086.4
Akbarnagar, b	8.30	122.4	1867	170	72	1030	0	3261.4
Ersapally, a	8.50	122.4	1991	99	65	720	0	2998.4
Pandu, a	8.40	122.4	1742	71	18	833	20	2806.4
Pandu, b	8.50	122.4	1867	78	0	1000	59	3126.4
Pandu, c	8.50	122.4	1493	64	48	625	0	2352.4
Pandu, d	8.40	122.4	1742	78	24	749	69	2784.4

* In parts per million of fresh fluid. No SO_4 and only traces of Ca found in any of the samples.

TABLE 4

Exchangeable bases in fluid from quagmires

VILLAGE	Ca	Mg	Na	K	TOTAL	Na AS PER CENT OF TOTAL
	*me.**	*me.*	*me.*	*me.*	*me.*	
Akbarnagar	18.55	4.76	12.12	1.11	36.54	34.73
Ersapally	15.29	2.23	13.55	1.25	32.32	41.87
Pandu	20.69	6.59	10.23	0.93	38.44	26.61

* me. = per 100 gm. air-dried ejecta passed through a 2-mm. sieve.

By the continued action of such a soil solution, the clay is alkalinized and saturated with sodium, which renders it highly dispersive and deflocculated. In the presence of a considerable excess of water, the dispersed soil material in the quagmire is in the form of a sol. The relative proportion of the exchangeable bases in the fluids is given in table 4. Obviously, the quagmires are sodium soils. The high content of exchangeable sodium is responsible for the deterioration of the structure of the soil. The high alkaline reaction of the fluid is due to the formation of soda, as explained by Gedroiz. The adsorbed sodium in the colloidal complex is hydrolyzed to NaOH, which combines with the CO_2 of the soil to form Na_2CO_3.

When wet, the quagmire is active. In this stage it ejects fluid during and after the rainy season. After several years, the activity ceases, and the quagmire becomes latent. The soil material then dries to a hard, crusty mass, and the quagmire looks like a cone-shaped crater.

The quagmire is a type of solonetz formed under specific conditions of topography and drainage. It is not a recent formation. The introduction of irrigation two decades ago intensified the process and increased the rate of its development.

The following morphological descriptions of five soil profiles studied along the slope of a quagmire-pervaded land under reclamation illustrate the process of quagmire formation:

Profile 1

The natural vegetation consists of stunted *Ischaemum pilosum* ("Kunda" grass) growing in clumps. The moisture content is high, increasing with depth. Lime and manganese nodules are freely distributed. A few yellowish quartz pebbles are present here and there. There is no water table at a depth of 7 feet.

0–60 inches	Dark gray clay with sand intrusions. Faint lentil structure between 24 and 42 inches, otherwise lumpy. The clay, to a depth of 36 inches, does not effervesce with acid; below, it is feebly effervescent.
60–72 inches	Merging of horizons. Pale yellowish gray clay feebly effervescent with acid. A few soft white lime concretions present.
72–>84 inches	Yellowish clay, moist, massive, and impeded. Many fist-like lime concretions present.

Profile 2

The natural vegetation consists of sparse patchy *Ischaemum pilosum*. On exposure and drying, the profile exhibits a highly cracked pattern. There is no water table at a depth of 6½ feet.

0–52 inches	Black clay becoming lighter in color with depth. Fairly moist, the moisture content increasing with depth. There is a free distribution of dark and white fine lime nodules. The clay does not effervesce with acid. It is very hard and compact except between 6 and 12 inches, where it is friable. From 12–24 inches it has a prismatic structure; between 24 and 36 inches it has a faintly lentil structure. Gypsum crystals are present in abundance between 36 and 52 inches.
52–60 inches	Merging of horizons. Yellowish gray clay, massive, very hard and compact. Does not effervesce with acid. A few large (2 inches thick) lime concretions present. Gypsum in crystalline form is absent below 52 inches. On drying there is a slight white salt efflorescence.
60–>76 inches	A distinct, differently colored horizon. Yellowish clay, massive, hard, compact, and impeded. Effervesces feebly with

acid. Many gray splotches. There is a free distribution of large hard white lime concretions.

Profile 3 (active quaqmire)

This is an active quagmire ripped open during summer. An iron crowbar 8 feet long easily slips completely into it. The surface of the quagmire is white as a result of salt incrustation and fine-sand accumulation. It is void of any kind of vegetation. Around the quagmire there is a growth of salt-loving grasses. There is slight fine-sand admixture below 24 inches. Water is struck 3½ feet below the surface. Below 6 inches, the clay as a whole caves in.

0– 5 inches	White sandy clay, dry and strongly effervescent with acid.
5–36 inches	Gray clay, very moist, highly sticky, compact, and structureless. There is feeble effervescence with acid. On exposure, the clay quickly turns black.
36–>42 inches	Same as above but heavily charged with lime. The clay effervesces very strongly with acid.

Profile 4

This is similar to profile 2. There is a fairly good vegetative cover of *Cynadon dactylon* ("Hariyali" grass) and *Ischaemum pilosum.* The soil to a depth of 4 feet is clay loam, grayish black, hard, and compact. The clay is sticky when moistened and becomes very heavy with depth. In the profile there is a free distribution of white lime and black manganese nodules. A few angular quartz pieces are also present. There is no water table at a depth of 6 feet.

0– 4 inches	Strong effervescence with acid.
4–10 inches	No effervescence with acid.
10–22 inches	Feeble effervescence with acid.
22–48 inches	Feeble effervescence with acid. Faintly lentil structure.
48–66 inches	A distinctly different horizon. Yellowish calcareous clay, moist, sticky, and massive. Abundant hard white lime concretions present.
66–>72 inches	Yellowish disintegrating rock, splotched with gray lime. Moist, sticky, and impervious. Strongly calcareous.

Profile 5

Sheet erosion is severe. Quartz pebbles are freely encountered on the land surface. A few granitic boulders lie exposed in the soil. *Ischaemum pilosum* grows in clumps and patches. There are a few tiny plants of *Acacia arabica* ("Babul"). To a depth of 30 inches, the soil effervesces feebly with acid; below, effervescence is very strong. There is no water table at a depth of 5½ feet.

0– 4 inches	Gray sandy clay loam, fairly dry.
4–12 inches	Grayish black clay, moist and compact.
12–36 inches	Grayish black clay of fair moisture content. Prismatic structure. From 18 inches downward, there are small shiny salt crystals. There are a few pockets of salt around 36 inches.

36–50 inches	Grayish black clay becoming lighter in color with depth. Rather moist and sticky. Faintly convex lentil structure.
50–60 inches	Yellowish gray plastic clay. Strongly effervescent with acid. Some lime concretions present.
60–>66 inches	Yellow clay, massive, impeded, and strongly calcareous. Highly sticky when moistened.

The five profiles are illustrated in figure 7. The soil is of the deep black cotton type having a salt and lime accumulation zone in the subsoil. The surface soil, 12 to 24 inches thick, becomes heavier in texture with the downward slope of the land, varying from sandy clay to clay loam and clay. It is cloddy, tough, and impeded. The subsoil, 26 to 48 inches thick, is prismatic cloddy to faintly lentil structured clay, favoring appreciable lateral drainage. This is underlin by hard and impervious granitic parent material. The surface of this rocky substratum is in the form of a trough. As the slope of the land is good and the surface soil is impervious, most of the rain water is carried away as surface runoff, little percolating downward. The salt-laden seepage from the subsoil of the adjoining elevated red soil area, however, runs laterally through the fairly pervious subsoil overlying the impervious substratum and accumulates in the trough-shaped mantle of the substratum to form a water pocket. The concretionary layer of alkaline material and the clay in the subsoil imbibe a large quantity of water. Thus the volume is increased when saturation occurs, slush is formed and finally erupts into quagmires.

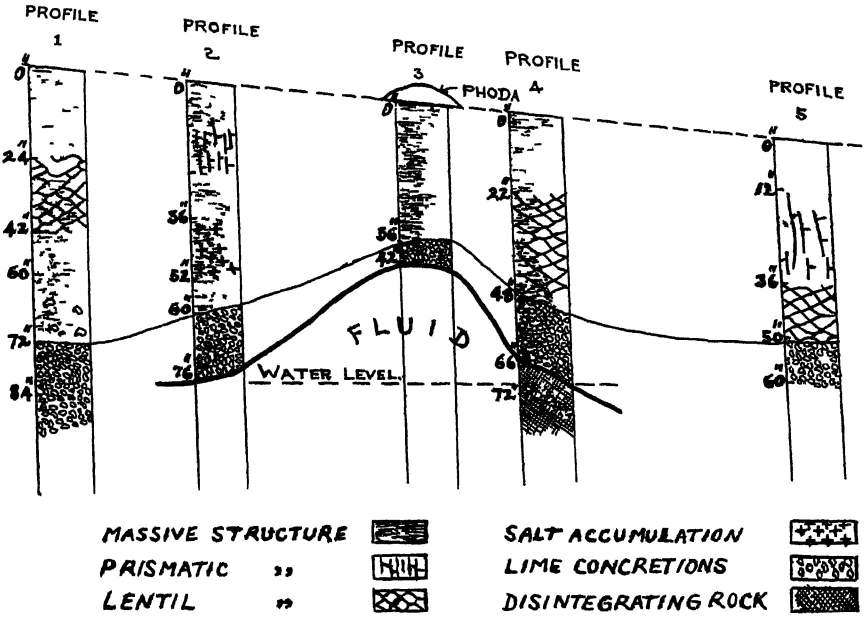

FIG. 7. FIVE SOIL PROFILES STUDIED ALONG THE SLOPE OF QUAGMIRE-PERVADED LAND, AKBARNAGAR VILLAGE, NIZAMSAGAR PROJECT

RED AND BLACK SOILS AND THEIR RELATION TO QUAGMIRE FORMATION

The adjoining red and black soils are formed on the same granitoid-gneissic parent material. Red soils occupy the elevated hilly areas of the macrorelief and microrelief of the project tract. The red soils are the normal soils. They have developed under free drainage and are residual. The black soils have developed under restricted drainage and are cumulose[4] or transported. In red soils, the products of weathering are thoroughly leached away. In black soils, only a small quantity is lost; in fact, the black soils are enriched with the products leached from the elevated red soils.

The sandy clays lie below sandy loams when only these two classes of soil occur or between sandy loams and clays when all three classes are present.

Sodium is the first base to be released by weathering, and the sandy loams are depleted of it because of their light texture and efficient drainage. It is transported to the immediately adjoining sandy clays. Initially, much sodium enters the colloidal complex of the sandy clay soils. At this stage of weathering, the clay, on absorption of water, swells as a result of deflocculation, which makes the soil massive. During summer periods there is intense desiccation, and the clayey soil is fragmented as a result of evaporation of moisture and shrinkage. With the process of fragmentation, cleaving takes place. This improves drainage. Weathering is intense because of the alternating wet and dry seasons. When, later, calcium comes into the soil solution, the sodium that has entered the colloidal complex is gradually replaced by calcium, and the clay is transformed into a calcium clay, which ultimately forms the typical calcium-saturated productive clay soils. The replacement of sodium by calcium also facilitates formation of a favorable structure by tending to flocculate the clay into granules and thereby improving its permeability.

Quagmires are formed in all the textural classes of soil—sandy loams, sandy clays, and clays. The prerequisite for their formation is impediment to the flow of salt-laden underground seepage. Pocket-like depressions, the junction of different textured soils, and the middle portions of vast slopes favor their development.

In sandy loams, quagmires develop in basin-shaped depressions where drainage is utterly lacking and on sloping plains where geologic conditions favor their formation. They form especially at the contact zone of the sandy loams and the sandy clays. Here conditions favoring formation of quagmires are the sudden infiltration of abundant material readily transported from the higher loose-textured sandy loams and the sudden heavy texture and imperviousness of the sandy clays. The quagmires that develop in sandy clay regions continue to be active as long as subsoil drainage remains retarded, and they become latent when the drainage becomes well established.

Quagmires are not encountered in the river border clays, as these are markedly permeable and thoroughly drained.

[4] Krishna, P. G. Soils of Gangawathi. Report on the Agricultural Survey of the Tungabhadra Project Area, Hyderabad State, India, by J. B. Mehta. 1933.

REMEDIAL MEASURES

Measures to check quagmire formation and to reclaim quagmire-pervaded lands are imperative in view of the menance to agriculture and the danger to livestock, for animals not uncommonly sink bodily and perish in active quagmires.

As drainage in quagmire-pervaded lands is very bad, the first step should be to provide an efficient drainage system. The efficient working of a subsoil drain in quaggy land is illustrated in figure 8. Several small artificial ponds, which since the introduction of canal irrigation in the Nizamsagar tract have served no useful purpose but only caused waterlogging, should be breached. Canals and distributaries should be lined in places where there is much seepage, especially where they run on embankments or in cuttings of soil laden with soluble alkali salts. Wells may be sunk at suitable places for pumping out water to relieve waterlogging. To avoid alkaline subsoil waters, these waters should be analyzed prior to location of sites for large wells. Salt resistant varieties of sugar-cane[5] must be cultivated in areas commanded by such wells. Ample provision for culverts and water channels should be made when diking is resorted to for laying out railway lines, roads, or even canals and distributaries that interfere with the natural drainage.

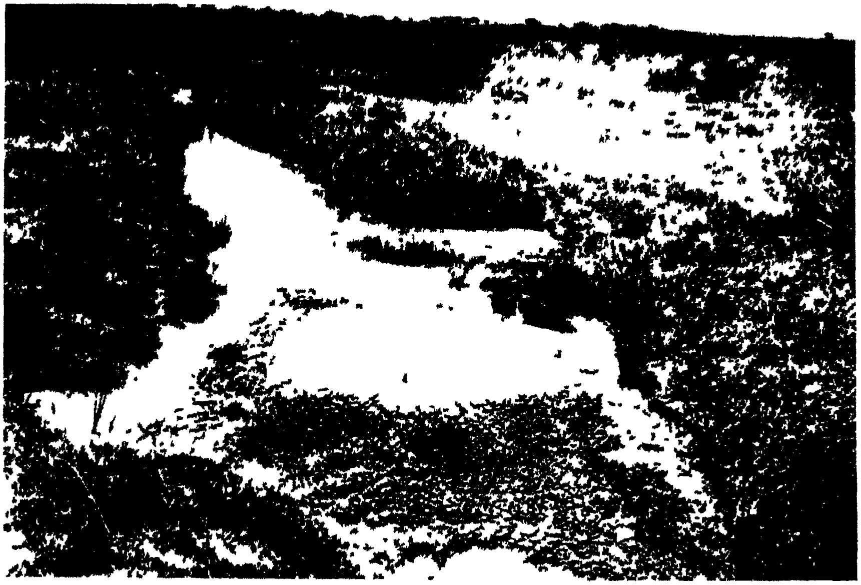

FIG. 8. AN EFFECTIVE DRAIN IN QUAGGY LAND

The quagmire lands should be subjected to proper reclamation treatment for reducing the alkalinity. Addition of large quantities of bulky organic manures would improve the physical condition of the soil. Gypsum should be applied to prevent formation of alkali carbonate (Na_2CO_3) and reduce alkalinity. It may be mixed, at the rate of 200 to 300 pounds per acre, with manure to be distributed on such soils. Large applications of gypsum would have to be made to soils that are very strongly alkaline. In the reclamation of quagmire-pervaded lands, 1 ton of gypsum per acre would have to be applied.

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[5] Krishna, P. G Investigations on the alkalinity and saltiness in Gur (Jaggery) made from Coimbatore sugarcane varieties. *Indian Jour. Agr. Sci.* 19(1): 163–179. 1949.

CHANGES INDUCED IN SOIL BY ETHYLENE OXIDE STERILIZATION

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Received for publication March 13, 1950

Steam under pressure serves adequately to rid soil of viable organisms, but such treatment may cause alterations in the structure, organic matter, or concentration of soluble salts in the soil. In consequence, heat treatment may make soils either more or less favorable for the growth of soil microorganisms or of higher plants. A method of sterilizing soil without changing its inherent characteristics is greatly to be desired.

Roberts *et al.* (6) reported in 1943 that ethylene oxide vapor could be used to sterilize soil completely, and that soluble salts were not increased during the sterilization process. Recently, Dalton and Hurwitz (2) have confirmed the efficacy of ethylene oxide as a soil-sterilizing agent, and have noted that its use induced little change in amount of ammonium-acetate-soluble copper and manganese in soil. A general review of the sterilizing action of gaseous ethylene oxide has been prepared by Phillips and Kaye (5).

Both the ease of application of ethylene oxide vapor and the apparent lack of undesirable changes in soil properties led to efforts to evaluate this means of soil sterilization. It was quickly noted that the microbial production of carbon dioxide from soil sterilized with ethylene oxide and then reinoculated greatly exceeded that produced either from untreated for from steam-sterilized lots of the same soil (1). Apparently there was a severalfold increase in the amount of carbonaceous material readily available for microbial utilization. Concurrently, Allison[2] noted that sterilization of soils with ethylene oxide raised their pH values.

This paper presents some observations of the effect of treatment with ethylene oxide on the total carbon, pH, and readily available phosphorus values of prairie soils and on the carbon dioxide evolution from such soils when incubated moist following treatment.

MATERIALS AND METHODS

Locally collected prairie soils were air-dried and screened initially. Individual soil portions of 100 to 500 gm. in shallow layers were exposed to ethylene oxide vapor within a pressure-style aluminum cooker of 9 l. capacity and with the lid refitted with three brass petcocks. One petcock was connected to a vacuum pump, a second to a vacuum gauge, and a third to a small cylindrical funnel through which known amounts of ethylene oxide could be introduced. Prior to introduction of ethylene oxide, the initial atmosphere was evacuated. The moisture status of soil lots during exposure, atmospheres of ethylene oxide used, and duration of exposure are noted in conjunction with the experimental observations. After exposure, all soil lots were thoroughly aerated, to remove traces of ethylene oxide vapor, which otherwise might interfere with microbial recolonization.

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[1] U. S. Department of Agriculture and Iowa Agricultural Experiment Station, cooperating. Journal Paper no. J-1749, Project 965, of the Iowa Agricultural Experiment Station.

[2] Allison, L. E. Unpublished report of the U. S. Regional Salinity Laboratory, Riverside, California. 1949.

For respiration studies, 100-gm. soil portions, in triplicate, were maintained in rubber-stoppered 500-ml. conical flasks, connected to a moisture-saturated, CO_2-free air stream. The outgoing air stream was passed through standard alkali for continuous collection of CO_2. Prior to incubation, soil lots were watered to bring them to 50 cm. of moisture tension and inoculated with 1 gm. of freshly collected soil. Check soil lots were similarly inoculated. Incubation was at 30°C., usually for 2 weeks.

Total carbon was determined by the dry combustion method. Readily available phosphorus was taken as that obtained by shaking 1 gm. of soil in 7 ml. of 0.03 N NH_4F in 0.025 N HCl for 1 minute. Phosphorus content of the extract was determined by the method of Dickman and Bray. The pH was determined by means of a glass electrode.

TABLE 1

Cumulative carbon dioxide evolution from unsterilized, steam-sterilized, and ethylene-oxide sterilized soil lots

INITIAL SOIL TREATMENT	CO_2 EVOLVED* PER 100 GM. SOIL DURING INCUBATION PERIODS						
	1 day	2 days	4 days	6 days	8 days	10 days	14 days
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
None	23	39	71	88	110	116	144
Steam (15 p.s.i., 30″)	27	61	100	122	143	155	181
Ethylene oxide	10	60	229	366	495	531	600

*Values given are averages of three replicates.

RESULTS

Cumulative amounts of carbon dioxide evolved during incubation by untreated, steam-sterilized, and ethylene-oxide-treated aliquots of Wabash silty clay shown in table 1. The ethylene oxide treatment in this instance consisted of exposure of air-dry soil to 0.5 atmosphere of the vapor for 16 hours. In a score of other comparisons, employing Clarion loam, Webster silt loam, or Wabash silty clay, severalfold increases in the carbon dioxide output of soils were noted following treatment with ethylene oxide.

Total carbon determinations made on untreated and on certain ethylene-oxide-treated soil lots are shown in table 2. Following gaseous treatment but prior to carbon analyses, the Webster samples were incubated for 2 weeks, and during this incubation lost 0.16 per cent by weight of carbon as carbon dioxide. The Wabash samples were air-dried immediately following exposure and were stored 30 days prior to analysis.

The magnitude of the differences in total carbon content of untreated and of ethylene oxide treated soils suggested that gravimetric differences following treatment could easily be detected. Triplicate 10-gm. portions of oven-dried quartz sand, of Wabash silty clay, and of an acid (pH 4.6) marine clay parent material were placed in tared containers, moistened to 10 per cent, and exposed to 0.5 atmosphere of ethylene oxide for 24 hours. All materials were then dried at 90° C. and again weighed. The quartz sand, as well as weighing bottles containing 10 ml. of distilled water, failed to gain weight during their exposure to ethylene oxide. The Wabash silty clay showed a weight gain of 1.55 per cent, and the marine clay, of 12.27 per cent.

TABLE 2

Total carbon, available phosphorus, and pH values determined for certain soil lots treated with gaseous ethylene oxide

ETHYLENE OXIDE TREATMENT		SOIL MOISTURE DURING TREATMENT	TOTAL CARBON	READILY AVAILABLE PHOSPHORUS	pH
atmos.	*hours*	*per cent*	*per cent*	*ppm.*	
		Webster silt loam			
None	—	—	2.92	20.6	6.15
0.5	16	5.0	3.29	28.4	7.22
0.5	16	24.0	3.30	30.4	7.20
		Wabash silty clay			
None	—	—	2.84	9.3	6.30
0.2	16	5.5	3.01	12.2	6.81
0.2	16	25.0	3.43	12.3	6.76
0.8	16	5.5	3.55	12.4	7.40
0.8	16	25.0	3.88	12.7	7.76
4.0	48	10.0	4.12	15.4	8.14

TABLE 3

Carbon dioxide production by untreated and by ethylene-oxide-treated soil and by their leachates

SOIL TREATMENT	CO_2* PER 100 GM. SOIL
	mgm.
a. None (check)	168.6
b. As (a), but leached prior to incubation	172.0
c. 0.5 atmos. ethylene oxide for 16 hours	676.6
d. As (c), but leached prior to incubation	198.1
e. Untreated soil (100 gm.) plus leachate from 25 gm. untreated soil	165.4
f. As (e), but leachate boiled	166.6
g. Untreated soil (100 gm.) plus leachate from 25 gm. of ethylene oxide treated soil	349.9
h. As (g), but leachate boiled	336.0

* Values given are averages of three replicates, incubated 18 days.

The material added to soil during the course of ethylene oxide sterilization was easily removed by leaching. It persisted in soils or in leachates given heat treatment. The following experiment is illustrative: Air-dry Wabash silty clay was exposed to 0.5 atmosphere of ethylene oxide for 16 hours. Unexposed as well as exposed lots were leached with 1.6 times their weight of distilled water. Portions of each leachate were boiled until reduced to approximately one third their initial volume and then restored to volume with distilled water. Quantities of leachate corresponding to the amounts obtained from 25-gm. portions of soil were then added to 100-gm. lots of untreated soil for incubation. Amounts of carbon dioxide evolved from these lots as well as from unleached and leached soil lots are shown in table 3.

When treated soil was leached with distilled water, and the leachate concentrated by heating at 80° C. under reduced pressure, the concentrate obtained was a syrupy liquid, slightly sweetish to the taste. Upon dry combustion, this crude material yielded 115 per cent of its own weight of carbon dioxide. When added to soil, the concentrate increased carbon dioxide evolution therefrom by an amount roughly equivalent to that obtained by adding an equal weight of technical ethylene glycol.

The observation by Allison that ethylene oxide treatment raises the pH value of soil was confirmed. The pH values given in table 2 show the extent to which ethylene oxide treatment changed the reaction of certain of the soils employed. Differences in pH values due to treatment persisted in soils during prolonged laboratory storage.

The amounts of readily available phosphorus determined for certain soil lots prior to and following treatment with ethylene oxide are shown in table 2. The Webster soil was incubated moist for 2 weeks at 30° C. before being dried and stored for analysis. The Wabash samples were air-dried immediately following treatment and stored for 3 months before analysis.

DISCUSSION

Phillips and Kaye (5) have pointed out that ethylene oxide does not hydrolyze readily to form ethylene glycol, and they question whether glycol formation has any connection with its sterilizing action. Its hydrolysis is facilitated by the presence of the hydrogen ion or by high salt concentration, and Phillips (4) has suggested that, in the sterilization process, ethylene oxide reacts with groups in the protein molecule, such as the hydroxyl, sulfhydryl, amino, or carboxyl, which contain a labile hydrogen atom. Kaye and Phillips (3) found that gaseous ethylene oxide sterilized relatively dry objects better than relatively moist ones.

The higher total carbon contents noted in the current work for soils given ethylene oxide treatment, the persistence of this added carbonaceous material following either heating or prolonged laboratory storage, and its ready availability for microbial utilization indicate that ethylene oxide reacts in soil to form some stable, nongermicidal compound. The gravimetric studies showed that neither quartz sand nor distilled water catalyzed the reaction involved, whereas in the presence of soil ethylene oxide was transformed into some nonvolatile compound that is readily utilized by microorganisms. Although the substance or substances formed in soil during the course of ethylene oxide sterilization were not identified, it is quite probable that in the presence of soil, ethylene oxide is hydrolyzed to ethylene glycol.

Accompanying the increase in content of readily available energy material in soil during ethylene oxide treatment, there are increases in readily soluble phosphorus and in pH values. Therefore, although ethylene oxide may offer certain advantages over heat or other treatments for the sterilization of soil, it is nevertheless not an ideal sterilizing agent, as it fails to provide a sterile soil which differs from the initial soil only in the absence of viable organisms.

SUMMARY

Sterilization of soils by means of gaseous ethylene oxide greatly increased their total carbon content. The added carbonaceous material was readily available for microbial utilization; fivefold increases in carbon dioxide production were noted for the first few days of incubation of soil following exposure to ethylene oxide vapor. Ethylene oxide treatment was also observed to raise the pH and the readily available phosphorus values in soil.

The energy-yielding material found in soils following their exposure to ethylene oxide was easily leached by water, and it was not destroyed by boiling at 100° C. It was not found in distilled water or in quartz sand exposed to ethylene oxide vapor. It is suggested that soil functions as a catalyst for the hydrolysis of ethylene oxide.

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(3) Kaye, S., and Phillips, C. R. 1949 The sterilizing action of gaseous ethylene oxide. IV. *Amer. Jour. Hyg.* 50: 296-306.

(4) Phillips, C. R. 1949 The sterilizing action of gaseous ethylene oxide: II. *Amer. Jour. Hyg.* 50: 280-288.

(5) Phillips, C. R., and Kaye, S. 1949 The sterilizing action of gaseous ethylene oxide: I. *Amer. Jour. Hyg.* 50: 270-279.

(6) Roberts, J. L., et al. 1943 Preliminary studies on soil sterilization with ethylene oxide. *Jour. Bact.* 45: 40.

METHODS OF ESTIMATING APPARENT DENSITY OF DISCRETE SOIL GRAINS AND AGGREGATES[1]

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Received for publication March 24, 1950

In an attempt to estimate the relative erodibility of soils by wind, a need arose for a method of determining the apparent density of the various fractions that are moved by the wind. A perusal of the available literature failed to indicate any method that could be used for this purpose. Several methods have been recommended for measuring the bulk density, or volume weight, of the undisturbed soil bed (2, 3, 4, 7). Likewise, detailed information is available on how best to determine the apparent density of discrete soil clods or large aggregates (5, 6). None of the methods examined, however, are applicable for determining the apparent density of small particles such as those eroded by wind or by water. The size of fraction eroded by wind is usually appreciably smaller than 2 mm. in diameter. The erodibility of these fractions is markedly affected by their apparent density. Four methods were, therefore, studied for estimating the apparent density of small soil particles or aggregates. A description of these methods together with a discussion of the relative merits of each is included herein.

SAMPLING SOILS FOR ANALYSIS OF APPARENT DENSITY

To disturb the structure as little as possible, the soils to be tested in the laboratory were taken from the field only when in a reasonably dry condition. A square-cornered spade was pushed under a soil layer of desired thickness. The soil was placed in a shallow tray and brought to the laboratory for thorough air-drying. After drying, the soils were separated into various size-fractions by dry-sieving on a set of rotary sieves.

PROCEDURE AND APPARATUS

The bulk density method

To measure the apparent density of grains or discrete aggregates in each soil fraction, a test tube of about 50-ml. capacity and an automatic tapping device were used (fig. 1). The test tube was approximately 6 inches high. One end of a paper sleeve 2 inches long and with inside diameter equal to the outside diameter of the test tube was fitted around the upper end of the test tube. Soil grains of a given diameter were poured in until the level of the bed was 0.5 to 1 inch above the top of the test tube. The test tube was then tapped on the tapping device until the weight of its contents, excluding the contents of the sleeve, was constant. The time required to reach the constant weight varied with the size of the

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[1] Contribution No. 420, department of agronomy, Kansas Agricultural Experiment Station, Manhattan, Kansas, and the Soil Conservation Service, U. S. Department of Agriculture. Cooperative investigations in the mechanics of wind erosion.

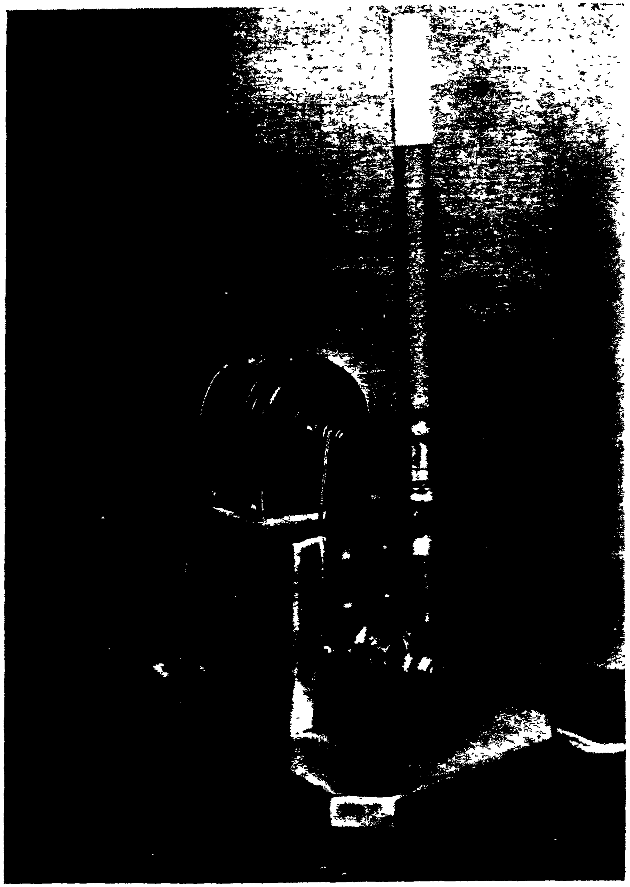

FIG. 1. AUTOMATIC TAPPING DEVICE FOR MEASURING BULK DENSITY OF SOIL GRAINS AND AGGREGATES

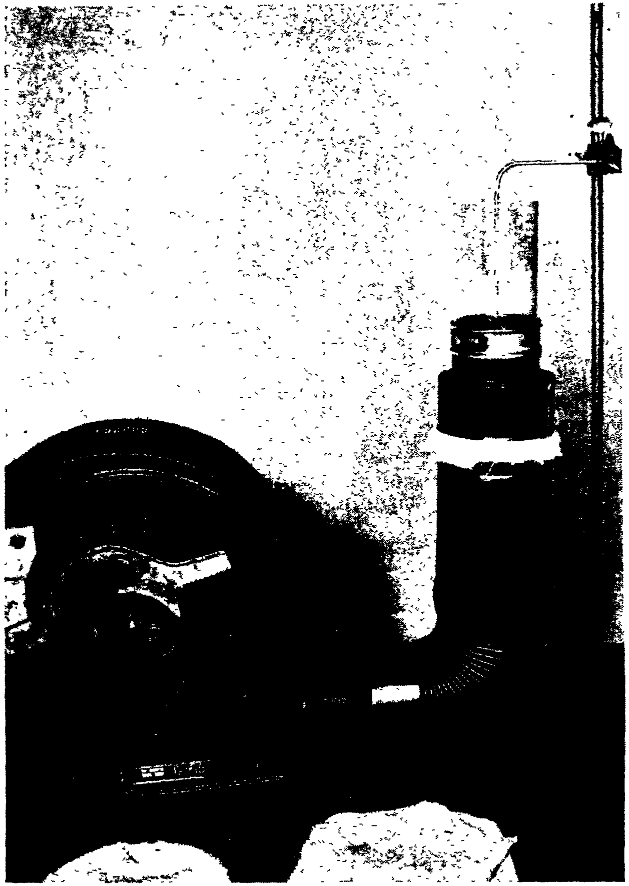

FIG. 2. APPARATUS FOR MEASURING EQUIVALENT APPARENT DENSITY OF SOIL AGGREGATES BY THE ELUTRIATION METHOD

aggregates, but in no case did it exceed 30 seconds. The contents of the full test tube were then weighed. To do this, it was necessary to pull the sleeve out and discard the surplus grains by sliding a straightedge level across the top of the test tube.

The tapping device is composed of a 1/100-horsepower electric motor connected to a spirally surfaced cam supporting a vertical rod on which a test tube and its contents rest vertically. The test tube rides inside a transparent vertical tube fixed to the frame of the device. For each turn of the cam the rod and the test tube are raised gradually, then allowed to drop of their own weight for a distance of $\frac{3}{8}$ inch. A flat piece of wood is mounted on top of the rod to absorb the shock exerted by the fallen test tube. The test tube receives 400 taps per minute.

Tapping by hand instead of on the automatic tapping device was carried out for comparison. The test tube and the upright sleeve were filled with the material to be tested. The bottom of the test tube, held vertically, was then tapped gently against a wooden table until no change in the level of the soil grains was observed. The contents of the full test tube were then weighed.

The bulk density of each size fraction separated by sieving was determined by dividing the thoroughly air-dry weight of the contents of the test tube by the volume of the test tube. The apparent density of the soil grains was estimated by dividing the bulk density by 1.53 and multiplying the quotient by 2.65. The constant 1.53 represents the bulk density of the oven-dry quartz sand of any sieve grade, and 2.65 represents the real and, presumably, the apparent density of the quartz grains. Both of these constants, as shown in a subsequent section of this report, were found to vary but little in the different samples of quartz sand that were analyzed.

The apparent density of all discrete grains or aggregates contained in the soil was determined by summing the products of the apparent density of each sieve grade and the percentage weight of the grade, and then dividing the sum by 100.

The elutriation method

The second method measures the equivalent apparent density of soil aggregates and is dependent on the vertical air stream required to barely lift the aggregates. The force required to lift the aggregates slightly exceeds the downward pull of gravity and for practical purposes may be considered equal to it. The force of gravity depends on the mass of the aggregate, whereas the force of the air stream required to lift the aggregate varies as the square of its velocity and is dependent on the size, shape, and apparent density of the aggregate. The minimal vertical velocity of the wind required to lift the aggregate, known as the vertical threshold velocity, can therefore be used to specify the equivalent size, shape, and apparent density of the aggregates. The size is known from sieving. It is only necessary, therefore, to determine the apparent density and shape. It is virtually impossible to describe a shape such as that of a natural soil aggregate or to determine with this method its effect independently of apparent density. Hence, the equivalent apparent density was computed. The equivalent apparent density may be defined as the apparent density of an imaginary soil aggregate which has the same diameter as the actual soil aggregate but which has a shape similar to standard dune sand grains. Quartz sand and pebbles of uniform shape and density for grains ranging up to 6.4 mm. in diameter were used as a standard in measuring the equivalent apparent density of the soil aggregates.

Since the force required to lift the soil aggregate varies as the square of the vertical wind velocity, it follows that the equivalent apparent density of the aggregate lifted by wind is equal to $\left(\frac{V_1}{V_2}\right)^2 \times 2.65$, where V_1 is the average vertical velocity of the air stream required to lift the soil aggregate and V_2 is the average vertical velocity of the air stream required to lift the quartz sand grain of 2.65 density and of the same size (sieve grade) as the soil aggregate. Slight differences between the shape of the soil aggregates and the sand grains were observed, and the effects of these differences, if any, presumably were reflected in the equivalent apparent density of the soil aggregates.

The apparatus used in this method consisted of a 3-inch diameter vertical duct connected to a blower run by an electric motor(fig. 2). Near the upper end of the duct various thicknesses of cloth filter, depending on the velocity of the wind required, were used. A few inches above the cloth filters a 300-mesh sieve was inserted, and on this sieve rested the grains of aggregates for which the lifting velocity was to be determined. Further control of the wind was obtained by varying the cross-sectional area of an air inlet opening. The pressure exerted against the cloth filters when the blower was on ranged from 1 to 10 inches of water. The pressure exerted against the sieve was equivalent to 0.2 to 4.5 inches of water. A sufficient pressure head was exerted against the sieve to produce a uniform velocity throughout the whole cross-sectional area in the duct immediately above the sieve where the soil grains were.

The horizontal threshold velocity method

The third method is based on the horizontal air stream required to initiate the movement of soil aggregates placed in a level bed of uniform thickness. A horizontal duct 4 feet long and 4 inches square was connected to a blower as in method 2. Cloth filters of varying degrees of porosity were used on the windward end of the duct to facilitate the control of stream velocity and especially to produce a uniform velocity throughout the whole cross-sectional area of the duct immediately to the lee of the filter. Further control of the air velocity was facilitated by adjusting the air intake opening to the blower. Air velocity was measured at a 2-inch height near the leeward end of the duct.

A velocity required to initiate the movement of the grains, known as the horizontal threshold velocity, was determined for beds of sand grains and of soil aggregates. For exposure to the wind, the soil or sand sample was placed in a shallow, rectangular trough and the sample was smoothed with a straightedge level with the top of the trough. The equivalent apparent density of the soil aggregates, ρ_1, was computed from the average threshold velocities in accordance with the expression $\rho_1 = \left(\frac{v_1}{v_2}\right)^2 \times 2.65$, where v_1 is the average threshold velocity of the soil aggregates and v_2 is the average threshold velocity of the quartz grains of 2.65 density. The average threshold velocity was determined by averaging the velocity required to move only the most erodible grains with the minimal velocity required to produce a continuous movement of all grains contained in the sample. The former velocity is known as the minimal threshold velocity, the latter as the maximal threshold velocity. The difference between the minimal and the maximal threshold velocities for the small grains was virtually nil. The difference increased directly with the size of the grain, however, reaching a maximum of 5 miles per hour for quartz grains approaching 2 mm. in diameter.

TABLE 1

Real density of quartz sand and gravel as determined by the standard pycnometer method

DIAMETER OF GRAINS	REAL DENSITY			
	Ottawa sand		Series B	
	1	2	1	2
mm.				
<0.1			2.65	2.66
0.1–0.15	2.64	2.66	2.64	2.65
0.15–0.25	2.65	2.66	2.63	2.64
0.25–0.42	2.65	2.65	2.63	2.62
0.49–0.59	2.66	2.66	2.62	2.64
0.59–0.84	2.65	2.65	2.62	2.62
0.84–1.19			2.62	2.61
1.19–2.0			2.61	2.61
2.0–6.4			2.61	2.60
Average	2.65	2.66	2.63	2.63

The individual grain weight method

At least 1,000 quartz sand grains and an equal number of soil grains or aggregates from each sieve grade were counted and weighed. The apparent density of the soil aggregates was then computed. The apparent density is equal to 2.65 $\frac{W_1}{W_2}$ where W_1 is the weight of a number of soil grains and W_2 is the weight of an equal number of the same-sized quartz sand grains of 2.65 apparent density.

ANALYTICAL RESULTS

The erodibility of soil particles or aggregates is dependent on their mass. The mass of the aggregates is in turn dependent on their size, shape, and apparent density. The apparent density is dependent on the volume of the pores within the aggregates and on the real density of the soil material of which the aggregates are composed. Both the real density and the volume of the pores within the soil aggregates vary appreciably in different soils. The real density of quartz grains, on the other hand, varies little and is generally accepted as 2.65.

The real density of the quartz grains (table 1) was found to be about the same for all grain sizes, at least up to 6.4 mm. in diameter, and varied little from the generally accepted value of 2.65. The apparent density for the larger grains as determined by the method of Russell and Belcerek (5) likewise varied little from the average value of 2.65. The value of apparent density in six replicated determinations ranged from 2.57 to 2.68, giving an average value of 2.63, which was identical with the average value of the real density of these grains. The volume of the pores, at least within larger grains of quartz sand and gravel, was evidently nil, or almost nil.

The bulk density of quartz sand was likewise found to be almost the same for any size of grain and was about the same in the different samples analyzed (table 2). This serves as further proof of the relative absence of pores within quartz grains. The bulk density of quartz sand of any sieve grade was about 1.53. The constancy of the bulk density of quartz sand seems to indicate that the shape of the grains and the volume of the interstices between the grains are constant for any uniform size of grains of which a bed is composed.

TABLE 2

Bulk density of quartz sand and gravel of various sieve grades

DIAMETER OF GRAINS	BULK DENSITY*								
	Ottawa sand		Series A		Series B		Series C		AVERAGE
	1	2	1	2	1	2	1	2	
mm.									
<0.1			1.50	1.49	1.48	1.49	1.49	1.50	1.49
0.1 -0.15	1.55	1.58	1.51	1.51	1.42	1.42	1.42	1.43	1.48
0.15-0.25	1.50	1.50	1.57	1.49	1.45	1.44	1.46	1.45	1.48
0.25-0.42	1.55	1.54	1.60	1.58	1.50	1.51	1.54	1.42	1.53
0.42-0.59	1.57	1.58	1.64	1.62	1.50	1.53	1.56	1.56	1.57
0.59-0.84	1.66	1.67	1.58	1.60	1.51	1.51	1.58	1.58	1.59
0.84-1.19			1.54	1.51	1.53	1.57	1.54	1.56	1.54
1.19-2.0			1.52	1.52	1.57	1.57	1.58	1.59	1.56
2.0 -6.4					1.50	1.50	1.45	1.45	1.48
Average..................	1.57	1.57	1.56	1.55	1.50	1.50	1.51	1.52	1.53

* Series A is based on a sample of sand from near Great Bend, B from near Rolla, and C from St. George, Kansas. Ottawa sand is based on two samples obtainable commercially, the A.S.T.M. standard graded sand and the A.S.T.M. 20- to 30-mesh standard sand.

Because of these virtually constant physical characteristics, quartz sand and pebbles were taken as a convenient standard in determining indirectly the apparent density of discrete soil grains or aggregates. In method 1 this was done by dividing the bulk density of a bed of soil aggregates by 1.53 and multiplying the quotient by 2.65. The constant 1.53 is the bulk density of quartz grains of any sieve grade, and 2.65 is the real and apparent density of the grains. In method 1 it was assumed that the volume of the interstices between the soil aggregates and between quartz grains of the same size was the same. The constancy in the bulk density of quartz sand and pebbles left no doubt that the volume of the interstices between quartz grains remained the same irrespective of the size of the grains of which the bed was composed. Whether the volume of the interstices between the soil aggregates remained constant, as with quartz grains, could not be determined directly.

In methods 2 and 3 the equivalent apparent density of the soil aggregates was determined from the relative vertical and horizontal threshold air velocities required to move quartz grains and to move soil aggregates. The shape of the aggregates on some soils differed somewhat from the shape of the quartz grains—the latter being less angular than the former. The variation in shape probably had some effect on the velocity of the air required to move the aggregates. This variation would, therefore, be reflected in the value of the equivalent apparent density of the aggregates.

TABLE 3

Comparison of bulk density determined with the automatic tapping device and by the hand method

DIAMETER OF GRAINS	BULK DENSITY					
	Tapped on tapping device			Tapped by hand		
	15 sec.	30 sec.	60 sec.	10 taps	20 taps	50 taps
mm.						
Quartz sand and pebbles						
<0.1	1.53	1.52	1.54	1.49	1.52	1.52
0.1 -0.15	1.42	1.42	1.43	1.43	1.46	1.46
0.15-0.25	1.43	1.44	1.44	1.46	1.47	1.47
0.25-0.42	1.47	1.47	1.47	1.49	1.51	1.52
0.42-0.59	1.49	1.50	1.49	1.54	1.54	1.56
0.59-0.84	1.50	1.51	1.48	1.61	1.61	1.62
0.84-1.19	1.52	1.51	1.51	1.51	1.55	1.56
1.19-2.0	1.55	1.54	1.54	1.53	1.55	1.58
Silt loam						
<0.1	1.27	1.32	1.32	1.26	1.31	1.32
0.1 -0.15	1.25	1.25	1.25	1.24	1.25	1.25
0.15-0.25	1.04	1.05	1.05	1.06	1.07	1.07
0.25-0.42	1.01	1.01	1.02	0.99	0.99	0.99
0.42-0.59	0.97	0.97	0.97	0.95	0.96	0.96
0.59-0.84	0.96	0.97	0.98	0.97	0.98	0.98
0.84-1.19	0.94	0.95	0.95	0.91	0.93	0.94
1.19-2.0	0.89	0.90	0.90	0.94	0.94	0,95

COMPARATIVE MERITS OF EACH METHOD

The automatic tapping device and tapping by hand in method 1 gave virtually the same values of bulk density of grain beds (table 3). About 30 seconds on the tapping device or 20 taps by hand against a wooden table were required to bring to a constant weight a given volume of the bed of any size of grain. No preceptible breakdown of soil aggregates was observed during the tapping process.

The apparent density of aggregates of three widely different soil classes is indicated in table 4 for method 1. The equivalent apparent density is shown in table 5 for method 2, and in table 6 for method 3. Table 7 gives a summary of the results of methods 1, 2, and 3.

TABLE 4

*Apparent density of soil aggregates determined from bulk density**

DIAMETER OF AGGREGATE	QUARTZ SAND AND PEBBLES		FINE SANDY LOAM		SILT LOAM		CLAY	
	Bulk density	Apparent density of grain	Bulk density	Apparent density of grain	Bulk density	Apparent density of grain	Bulk density	Apparent density of grain
mm.								
<0.1	1.49	2.58	1.33	2.30	1.32	2.29	1.18	2.04
0.1 -0.15	1.45	2.51	1.24	2.15	1.21	2.10	1.04	1.80
0.15-0.25	1.49	2.58	1.22	2.11	1.05	1.82	1.01	1.75
0.25-0.42	1.54	2.67	1.25	2.17	1.01	1.75	1.04	1.80
0.42-0.59	1.57	2.72	1.12	1.94	.99	1.72	1.01	1.75
0.59-0.84	1.56	2.70	1.05	1.82	.93	1.61	1.00	1.73
0.84-1.19	1.54	2.67	1.01	1.75	.97	1.68	.98	1.70
1.19-2.0	1.56	2.70	.91	1.58	.91	1.58	.97	1.68
2.0 -6.4	1.48	2.56	.86	1.49	.82	1.42	.86	1.49

* Apparent density of grain or aggregate is equal to $\frac{\sigma}{1.53} \times 2.65$, where σ is the bulk density of a bed of aggregates.

TABLE 5

*Equivalent apparent density of soil aggregates determined by the elutriation method**

DIAMETER OF AGGREGATES	V_2	FINE SANDY LOAM		SILT LOAM		CLAY	
		V_1	Equivalent apparent density	V_1	Equivalent apparent density	V_1	Equivalent apparent density
mm.	*m.p.h.*	*m.p.h.*		*m.p.h.*		*m.p.h.*	
<0.1	0.64	0.48	1.51	0.36	0.98	0.47	1.43
0.1-0.15	1.75	1.48	1.87	1.41	1.72	1.39	1.67
0.15-0.25	3.35	2.78	1.83	2.74	1.77	2.54	1.52
0.25-0.42	5.75	4.99	1.99	4.44	1.57	5.21	2.18
0.42-0.59	8.40	7.69	2.22	6.82	1.75	7.38	2.05
0.59-0.84	10.95	9.75	2.10	8.60	1.64	9.20	1.87
0.84-1.29	14.10	12.84	2.20	12.14	1.96	11.22	1.67
1.19-2.0	18.50	14.95	1.73	13.70	1.46	13.98	1.52
2.0-6.4	27.75	22.77	1.79	21.19	1.55	21.06	1.53

* Equivalent apparent density is equal to $\left(\frac{V_1}{V_2}\right) \times 2.65$, where V_1 is the vertical air velocity required to lift the soil aggregates and V_2 is the vertical air velocity required to lift quartz sand grains of the same size as the soil aggregates.

Method 4 was found quite unsatisfactory. Consequently, data obtained with this method are not presented. The counting of fine grains necessary for this method was tedius. The method was inaccurate unless at least 1,000 of the finer grains were used for determination. It was impossible to count large numbers of particles smaller than 0.25 mm. in diameter, hence the method was applicable

TABLE 6

*Equivalent apparent density of soil aggregates determined by the threshold wind velocity method**

DIAMETER OF AGGREGATES	V_2	FINE SANDY LOAM		SILT LOAM		CLAY	
		V_1	Equivalent apparent density	V_1	Equivalent apparent density	V_1	Equivalent apparent density
mm.	*m.p.h.*	*m.p.h.*		*m.p.h.*		*m.p.h.*	
<0.1	7.6	7.5	2.62	8.2	3.12	7.7	2.76
.1–.15	7.5	7.4	2.58	7.1	2.38	7.1	2.38
.15–.25	9.2	8.0	2.01	7.8	1.91	7.6	1.81
.25–.42	11.0	9.3	1.89	8.8	1.70	9.2	1.86
.42–.59	13.0	10.7	1.81	10.5	1.74	11.1	1.95
.59–.84	16.3	13.3	1.76	13.5	1.82	13.4	1.79
.84–1.19	21.9	17.9	1.77	17.3	1.65	17.7	1.73
1.19–2.0	39.1	29.3	1.48	28.7	1.43	30.3	1.59

* Equivalent apparent density is equal to $\left(\frac{v_1}{v_2}\right)^2 \times 2.65$, where v_1 is the threshold velocity required to erode the soil aggregates and v_2 is the threshold velocity required to erode quartz sand grains of the same size as the soil aggregates.

TABLE 7

Comparison of apparent density and equivalent apparent density of sand and soil aggregates determined by methods 1, 2, and 3

DIAMETER OF GRAINS	QUARTZ SAND AND GRAVEL			FINE SANDY LOAM			SILT LOAM			CLAY		
	Method			Method			Method			Method		
	1	2*	3*	1	2	3	1	2	3	1	2	3
mm.												
<0.1	2.58	2.65	2.65	2.30	1.51	2.62	2.29	0.98	3.12	2.04	1.43	2.76
0.1–0.15	2.51	2.65	2.65	2.15	1.87	2.58	2.10	1.72	2.38	1.80	1.67	2.38
0.15–0.25	2.58	2.65	2.65	2.11	1.83	2.01	1.82	1.77	1.91	1.75	1.52	1.81
0.25–0.42	2.67	2.65	2.65	2.17	1.99	1.89	1.75	1.57	1.70	1.80	2.18	1.86
0.42–0.59	2.72	2.65	2.65	1.94	2.22	1.81	1.72	1.75	1.74	1.75	2.05	1.95
0.59–0.84	2.70	2.65	2.65	1.82	2.10	1.76	1.61	1.64	1.82	1.73	1.87	1.79
0.84–1.19	2.67	2.65	2.65	1.75	2.20	1.77	1.68	1.96	1.65	1.70	1.67	1.73
1.19–2.0	2.70	2.65	2.65	1.58	1.73	1.48	1.58	1.46	1.43	1.68	1.52	1.59
2.0–6.4	2.56	2.65	2.65	1.49	1.79	†	1.42	1.55	†	1.49	1.53	†

* In methods 2 and 3 the density of quartz sand and gravel is assumed to be 2.65.

† Velocity required to erode this size of aggregate was unavailable.

only to discrete soil units greater than this diameter. The readiness with which fine grains become charged with static electricity made counting and handling virtually impossible.

The values for the apparent density obtained by method 1 and for the equivalent apparent density obtained by methods 2 and 3 differed, on the whole, very little for various aggregate sizes above 0.1 mm. in diameter (table 7). Two possible conclusions may be drawn as to why the agreement was good: first, that the differences, if any, between the shape of the aggregates and the shape of the standard quartz grains had no appreciable effect on the velocities of the air stream required to erode the aggregates; and second, that the effects of the differences in the shape of the aggregates were of the same magnitude and ran in the same direction for all sizes of aggregates and all soils used. The latter condition, as a case of coincidence, appears to be rather unlikely.

For particles smaller than 0.1 mm. in diameter, widely different results were obtained with each method and with each soil. This was to be expected in view of the differences in the physical composition of this fraction in each of the soils and in the nature of the measurement associated with each method of analysis. Method 1 perhaps comes closest to measuring the actual apparent density of these fine fractions. Methods 2 and 3 measure the vertical and the horizontal threshold air velocities, which are affected by shape, apparent density, and size distribution of the particles contained in this fraction. The so-called equivalent apparent density, which incorporates the effect of all three of these factors, is computed from the threshold velocities. The fraction smaller than 0.1 mm. did not represent the same size distribution of grains in each soil as did the other corresponding sieve grades. Silt loam contained the greatest amount of fine dust in this fraction (table 8), and sandy loam the least. The finest fractions would be most readily lifted by a vertical wind in method 2. This consequently would lower the value of the equivalent apparent density of this fraction. The finest fractions, on the contrary, as shown by previous experiments (1), would be most resistant to wind erosion as measured by method 3. This would tend to give a

TABLE 8

Size distribution and apparent density of the dry fractions contained in the sieve grade <0.1 mm. in diameter in different soils

PARTICLE DIAMETER*	QUARTZ SAND		FINE SANDY LOAM		SILT LOAM		CLAY	
	Size distribution	Apparent density of grain (assumed)	Size distribution	Apparent density of grain	Size distribution	Apparent density of grain	Size distribution	Apparent density of grain
mm.	%		%		%		%	
0.1–0.074	72.6	2.65	9.9	2.10	9.6	2.04	14.1	1.78
0.074–0.044	21.6	2.65	32.9	2.27	28.2	2.21	32.5	2.02
0.044–0.02	4.2	2.65	38.6	2.41	42.7	2.51	39.6	2.34
0.02–0.01	1.2	2.65	14.7	†	13.9	†	9.8	†
0.01–0.005	0.3	2.65	2.9	†	3.8	†	2.8	†
<0.005	0.1	2.65	1.0	†	1.8	†	1.2	†

* Particle diameter >0.044 mm. was determined by sieving, and that <0.044 mm. by rate of sedimentation in carbon tetrachloride. The particles <0.044 mm., therefore, represent the equivalent, rather than the actual diameter.

† Not enough to measure.

high value for the equivalent apparent density of this fraction. The results actually did run in this fashion. Thus, the silt loam fraction containing the greatest amount of fine dust showed the lowest equivalent apparent density by method 2 and the highest by method 3. On the other hand, the sandy loam fraction which contained the least amount of fine dust showed the highest corresponding value by method 3. All of the values obtained by methods 2 and 3 for fraction smaller than 0.1 mm. were either higher or lower than the corresponding apparent densities determined by method 1. Method 1 was the only method which appeared to be reasonably applicable to the whole range of size of fractions. Methods 2 and 3 were only applicable to sieve grades greater than 0.1 mm. in diameter. It is believed that all three methods would have given virtually the same values of equivalent apparent density had the size distribution in the finest sieve grade been the same in all cases compared.

Apart from the results with the smallest fractions, methods 1 and 3 agreed more closely than 1 and 2, or 2 and 3. Method 2 was apparently less accurate than the others, as judged by somewhat erratic values that were obtained. These apparent inaccuracies appear to be inherent in the method itself. A relatively large range of air velocity required to lift the lightest and the heaviest grains of any given fraction is mainly responsible for the inconsistency of the method. With method 3 no such wide range of velocity is encountered. For small grains of about 0.1 mm. in diameter in method 3 there is, in fact, but a single value of velocity that corresponds to the minimal and the maximal threshold for these grains. For the largest and the heaviest grains, the difference between the minimal and the maximal threshold did not exceed 5 miles per hour on a 40-mile-per-hour wind. The threshold velocities vary more or less directly with the average size, density, and shape of all of the component particles. On the other hand, in method 2, the velocity required to lift a given particle is fixed, irrespective of the size, shape, or amount of other particles contained in the mixture.

In method 1 it was assumed that the volume of the interstices between the soil aggregates or grains and between the standard quartz grains of the same sieve grade is the same. The values of apparent density obtained by methods 2 and 3 are not dependent on the variations in the volume of the interstices between the individual units. Yet the apparent density obtained by all three methods for aggregate sizes greater than 0.1 mm. came out virtually the same. These results prove that the assumption, at least within the range of soils studied, is true.

Each of the three methods indicated that the apparent density and the equivalent apparent density decreased with an increase in the size of the aggregates. This seems to indicate that the larger aggregates were more porous than the smaller ones. All three methods also indicate that fine sandy loam had the highest apparent density of all its aggregates above 0.1 mm., clay the intermediate, and silt loam the lowest.

CONCLUSIONS

Of the three methods of estimating the apparent density of soil grains or aggregates smaller than 6 mm. in diameter, method 1 appears to be the most desirable for the following reasons:

1. Measurements can be made quickly and simply.
2. The values obtained by this method are very consistent and apparently accurate.
3. The method is not subject to personal judgment or personal differences in handling if the automatic tapping device is used.
4. It is the only method examined that appears to be applicable for measuring the apparent density of the sieve grade smaller than 0.1 mm. in diameter.

In connection with erodibility studies, method 3 might be preferable to the other methods because it estimates the equivalent apparent density from direct measurement of actual erodibility. Method 2, on the other hand, is not based on measurement of actual erodibility. To estimate the equivalent apparent density reasonably accurately by method 2 or 3, the size of grains in quartz sand and in the soil samples that are being compared must be the same. In the sieve grade smaller than 0.1 mm. the size distribution was not the same in the samples examined, and, consequently, the estimated value of the equivalent apparent density was at wide variance with the actual value.

SUMMARY

Three methods of estimating the apparent density of erodible soil fractions were developed and compared: 1—the bulk density method; 2—the elutriation method; 3—the horizontal threshold velocity method.

Method 1 is the simplest and appears to be the only one of the three applicable to measuring the actual apparent density of any size of fraction separated by sieving.

Methods 2 and 3 measure the equivalent apparent density of discrete soil units. For sieve grades above 0.1 mm. in diameter all three methods gave virtually the same values. It was thus indicated that the noticeable variation in the shape of the discrete soil units had little, if any, effect on the threshold air velocities and on the value of the equivalent apparent density obtained therefrom. Method 2 was least consistent.

For the sieve grade below 0.1 mm. in diameter the three methods gave widely variable results. This was to be expected because the size distribution of the particles in this grade was not the same in all of the soils compared.

Method 4, based on weighing a definite number of quartz sand and soil grains, was tried and found impractical.

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PHYSICAL BASIS OF PARTICLE SIZE ANALYSIS BY THE HYDROMETER METHOD

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Received for publication April 8, 1950

The hydrometer method has been used extensively for many years, but its accuracy has often been questioned. The principal criticism has been that when a hydrometer is placed in a settling suspension a known interval of time after mixing, the density indicated on the stem cannot be associated with any particular level in the suspension and therefore cannot be related to a definite settling velocity. This indefiniteness prevents accurate determination of the sizes of the particles responsible for the observed density. On the other hand, it may be argued[1] that in any given measurement there will be a certain depth, which may be called the *effective depth*, where the density will be exactly equal to that indicated by the hydrometer. If a reliable method could be devised for determining the effective depth, Stokes' equation could be applied accurately, and the difficulty of determining particle size would be overcome. Because the determination of effective depth is an essential step in particle size analysis by the hydrometer method, an effort has been made to put this operation on a firm theoretical foundation.

THE DENSITY-DEPTH FUNCTION IN A SETTLING SUSPENSION

The following experiment was conducted[2] to obtain preliminary information on the variation of density with depth in suspensions of soil settling under the influence of gravity. A suspension of Dublin clay was prepared by shaking 50 gm. of the soil overnight, in a reciprocating shaker, with 150 ml. of water and 5 ml. of dispersing solution, consisting of 35.7 gm. of sodium metaphosphate and 7.9 gm. of sodium carbonate per liter. The suspension was transferred to a graduate, diluted with water to 1 liter, and thoroughly mixed. After a 2-hour settling period at a temperature of 28°C., aliquots containing 25 ml. each were taken at selected depths by the pipette method. The samples were dried and weighed, the weight of dispersing agent was deducted, and the concentration of suspended solids was calculated in grams per liter of suspension. In this way, a number of suspensions of the same soil were prepared and sampled. More than one aliquot was usually taken from each suspension, but samples were spaced widely to prevent overlapping, and deeper ones were taken first to avoid errors in the measurement of depth. The data are shown in table 1.

Using the function

$$c = k \log_{10} h + b, \qquad (1)$$

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[1] Thoreen, R. C. Comments on the hydrometer method of mechanical analysis. *Pub. Roads* 14: 93–105. 1933.

[2] The assistance of C. Krishnamoorthy in this experiment is gratefully acknowledged.

the empirical constants $k = 5.68$ and $b = 17.80$ gm. per liter were calculated from the data by the method of least squares. The curve plotted in figure 1 is a reproduction of the calculated curve. The experimental points indicate good agreement between the empirical function and the data from which it was derived.

TABLE 1

Concentration of suspended solids at various depths in a settling suspension

h	*c*	*h*	*c*	*h*	*c*	*h*	*c*	*h*	*c*
cm.	*gm./l.*	*cm.*	*gm./l.*	*cm.*	*gm./l.*	*cm.*	*gm./l.*	*cm.*	*gm./l.*
1	17.3	6	22.4	11	23.8	16	24.6	21	25.2
2	19.5	7	22.6	12	24.0	17	24.7	22	25.3
3	21.0	8	23.0	13	24.1	18	24.9	23	25.5
4	21.5	9	23.2	14	24.3	19	24.9	24	25.6
5	22.0	10	23.5	15	24.5	20	25.1	25	25.6

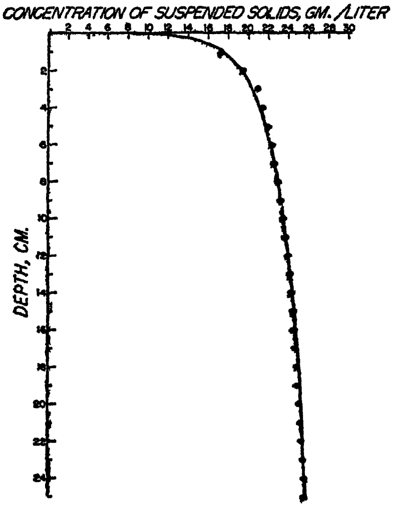

FIG. 1. CONCENTRATION OF SUSPENDED SOLIDS AT VARIOUS DEPTHS IN A SETTLING SUSPENSION

Curve drawn as a logarithmic function of depth, fitted by least squares

A functional relationship between density and depth[3] for this particular suspension having been found, it was considered possible that equation (*1*) might represent a general characteristic of soil suspensions undergoing sedimentation.

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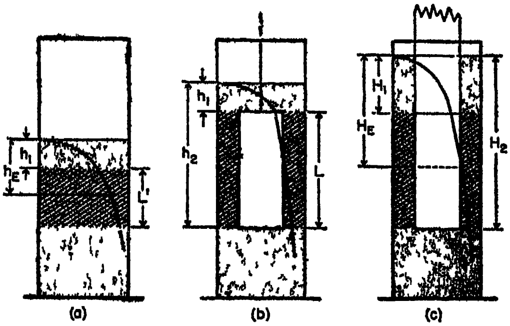
[3] Because of the linear relationship between density and concentration of suspension (Keen, "The physical properties of the soil", pp. 54–55), it was considered that for the purposes of this article it would be unnecessary to transform concentration values to density. Moreover, it may be shown, from the same principle, that a logarithmic concentration-depth function determines a logarithmic density-depth function; for this reason the density and concentration of suspension will be referred to interchangeably in the ensuing pages.

This idea was supported by the data previously published by Puri[4] and by Codoni[5], both of whom found density-depth curves similar to the one given in figure 1. It was tentatively assumed, therefore, that equation (*1*) would be generally applicable, and this hypothesis was used as the starting point in the development of a new hydrometer theory.

EFFECTIVE DEPTH OF A CYLINDRICAL HYDROMETER—SIMPLE CASE

It will now be proved that the effective depth of a cylindrical hydrometer may be accurately determined if the suspension in which it rests is of a type characterized by equation (*1*). It is convenient to deal first with cases in which the vessel is so large that the surface of the suspension will not be raised appreciably when the hydrometer is inserted. Because of the uniform cross-section of the hydrometer, the density which it registers will represent the average density of the suspension within the zone containing the bulb. The plane of average density must now be located, for it is this plane which determines the effective depth. On account of the curvilinear relationship between density and depth, the average density will not occur midway along the bulb, as assumed by Casagrande[6], but at a point that will depend upon the shape of the curve. In the following derivation it is convenient to use the concentration instead of the density for determining the effective depth. This procedure is justified by the fact that the plane of average concentration will coincide with the plane of average density because of the linear relation which exists between these two variables.



(a) ORIGINAL CONDITIONS (b) CONDITIONS AFTER INSERTION (c) HYPOTHETICAL CONDITIONS

FIG. 2. CHANGES IN LEVEL OF THE SUSPENSION AND CHANGES IN DENSITY GRADIENT CAUSED BY INSERTION OF HYDROMETER

Let h_1 and h_2 correspond to the depths of the upper and lower ends of the bulb beneath the surface (fig. 2). The average concentration ($\bar{c}$) may be computed as follows, using equation (*1*) for relating c to h:

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[4] Puri, A. N. A new type of hydrometer for the mechanical analysis of soils. *Soil Sci.* 33: 241–248 1932.

[5] Codoni, M. R. Density of soil suspensions and the use of densimeters for mechanical analysis. *Soil Sci.* 56. 7–18. 1943. The densimeter method of mechanical analysis. *Soil Sci.* 56: 423–431. 1943.

[6] Casagrande, A. Die Araometer-Methode zur Bestimmung der Kornverteilung von Boden und anderen Materialien. Julius Springer, Berlin. 1934.

$$\bar{c} = \left(\frac{1}{h_2 - h_1}\right) \cdot \int_{h_1}^{h_2} c\,dh = \left(\frac{1}{h_2 - h_1}\right) \cdot \int_{h_1}^{h_2} (k \log_{10} h + b)\,dh$$

By integration, it is found that

$$\bar{c} = k\left[\frac{h_2 \log_{10} h_2 - h_1 \log_{10} h_1}{h_2 - h_1} - \log_{10} e\right] + b \qquad (2)$$

The effective depth h_E, which represents the depth of the plane of average concentration, is related to $\bar{c}$ through equation (*1*). Hence, it may be written that

$$\bar{c} = k \log_{10} h_E + b \qquad (3)$$

If equation (*3*) is compared with equation (*2*), it becomes obvious that

$$\log_{10} h_E = \frac{h_2 \log_{10} h_2 - h_1 \log_{10} h_1}{h_2 - h_1} - \log_{10} e. \qquad (4)$$

This is the relationship sought, for it expresses the effective depth as a function of the depth of immersion. A significant feature of equation (*4*) is the fact that h_E is invariant with respect to k and b. That is, the effective depth corresponding to a given depth of immersion will depend only upon the general shape of the concentration-depth function, not upon the numerical values of the parameters which are found in individual cases.

Equation (*4*) is limited by the condition that the cross-sectional area of the sedimentation vessel must be very much greater than that of the hydrometer. This disadvantage may be overcome by a method described in the next section.

EFFECTIVE DEPTH OF A CYLINDRICAL HYDROMETER IN A NARROW CYLINDER OF SUSPENSION

The insertion of the hydrometer in a narrow sedimentation cylinder raises the level of the suspension and modifies the relationship between concentration and depth by redistributing the particles in the cylinder. These effects are evaluated quantitatively in the following paragraphs. It is assumed that the hydrometer will not be placed in the suspension until just prior to measurement, that it can be lowered into the suspension without turbulence, and that a negligbile amount of sedimentation will take place while the reading is being taken. Measurements made in the early moments of sedimentation will not meet these requirements and consequently will fall outside the scope of the present theory. As in the previous case, it is assumed that the segregation of the particles by their rates of fall in the suspension will result in a concentration gradient of the type given by equation (*1*).

The effect of placing the hydrometer in the suspension will be described with the help of figure 2. Let A represent the area of the sedimentation vessel and a the area of the hydrometer. When the hydrometer is inserted, the volume of the suspension which surrounds it will be equal to $L(A - a)$. This volume, indicated by the cross-hatching in figure 2b, will be called the "zone of measurement." Prior to insertion (fig. 2a), this same volume will have been confined to a narrower vertical zone. of thickness equal to L'. Therefore $L'A = LA - La$ and

$$\frac{L}{L'} = \frac{A}{A-a} \tag{5}$$

The ratio L/L', which will be designated by α, represents the linear magnification of scale produced by the encroachment of the hydrometer bulb. The rise in the level of the suspension will be equal to

$$h_0 = L - L' = L' \cdot \left(\frac{a}{A}\right) \tag{6}$$

As in the simple case, the hydrometer will register the average density in the zone of measurement. To calculate the effective depth it will be necessary to locate the plane of average density. This will require knowledge of the density-depth function. Because of the logarithmic density gradient existing prior to insertion of the hydrometer, the uniform lengthening of the column within the zone of measurement will produce a modified density-depth relationship which will also be a logarithmic function. Before any attempt is made to locate the plane of average density, the problem may be simplified by a hypothetical modification of conditions.

Suppose that the top of the hydrometer bulb were provided with a long extension consisting of a cylinder having the same cross-section as the bulb. Imagine this assembly to be lowered into the suspension until the bottom of the bulb occupies the same level as in the actual case. (See fig. 2c.) Under these hypothetical conditions, the enlargement of dimensions in the vertical direction will be uniform from the bottom of the hydrometer to the surface of the suspension, which will theoretically lie at a higher level than before. Moreover, the density will be a continuous logarithmic function of depth throughout the column, and will coincide with the actual density in the zone of measurement depicted in figure 2b. Therefore, all of the conditions necessary for the application of equation (4) are satisfied. Using the notation indicated in figure 2c, the effective depth (H_R) in the hypothetical case will be given by the following equation:

$$\log_{10} H_R = \frac{H_2 \log_{10} H_2 - H_1 \log_{10} H_1}{H_2 - H_1} - \log_{10} e. \tag{7}$$

Equation (7) locates the plane of average density with respect to the hypothetical level of suspension shown in figure 2c. To refer this to the surface of original suspension (fig. 2a), it will be helpful to imagine that the depth relations existing prior to insertion of the hydrometer, with its extension, can now be reproduced by removing it. In this operation all vertical dimensions would contract in the proportion $1/\alpha$.

Therefore

$$h_R = \frac{H_R}{\alpha} \tag{8}$$

and

$$\log_{10} h_E = \frac{H_2 \log_{10} H_2 - H_1 \log_{10} H_1}{H_2 - H_1} - \log_{10} ae, \tag{9}$$

where

$$H_1 = ah_1$$

and

$$H_2 = H_1 + L.$$

Equation (*9*) is an exact expression for the effective depth under the conditions originally specified. When the sedimentation vessel is very large, the coefficient a is equal to unity, and equation (*9*) reduces to equation (*4*). In both cases, the effective depth depends upon the functional relationship given in equation (*1*) but is independent of the numerical values of the parameters.

CONDITIONS AFFECTING ACCURACY

Ideal size distributions

The validity of the theory developed in the preceding paragraphs rests upon the hypothesis that the concentration of suspended solids is a logarithmic function of depth. A particular type of particle size distribution has been found which will satisfy this condition when the particles are thoroughly dispersed and allowed to settle in suspension. This distribution is characterized by an equal weight of particles within each size class in a geometric progression of sizes, and will be termed an *ideal distribution.* The ideal distribution is represented by a straight line on a conventional summation graph, where particle sizes are denoted by the logarithms of their diameters.

To establish the relationship between size distribution and concentration gradient, let P represent the summation percentage and d the particle size, and let m and n denote constants. The distribution may be represented by the equation

$$P = m \cdot \log_{10} d + n. \tag{10}$$

If the initial, or average, concentration of suspension is designated by c_0, and the concentration at depth h at time t by c,

$$P = \frac{c}{c_0} \times 100. \tag{11}$$

Therefore, by combining equations (*10*) and (*11*)

$$c = \left(\frac{c_0}{100} \cdot m\right) \log_{10} d + \left(\frac{c_0}{100} \cdot n\right). \tag{12}$$

Stokes' equation may be written in the form

$$d^2 = \left[\frac{18\eta}{gt(\sigma - \rho)}\right] h, \tag{13}$$

where η = viscosity of the medium, g = gravitational acceleration, σ = density of the solid, ρ = density of the liquid, t = time of fall (all in absolute CGS units).

By eliminating d from equations (*12*) and (*13*), it is found that

$$c = k \log_{10} h + b \tag{14}$$

in which

$$k = \frac{c_0}{100} \cdot \frac{m}{2},$$

and

$$b = \frac{c_0}{100}\left[n + \frac{m}{2}\log_{10}\frac{18\eta}{gt(\sigma - \rho)}\right].$$

Equation (*14*) is identical with equation (*1*), the empirical equation applied to the experimental data of table 1.

The preceding derivation justifies the conclusion that a soil having the ideal type of size distribution defined by equation (*10*), when dispersed in water and allowed to settle for an arbitrary interval of time, will give the logarithmic type of density gradient required in the theory. Before the results are applied directly to hydrometer measurements, it will be advantageous to consider other types of particle size distributions.

Nonideal size distributions

From the point of view of the theory, the size distribution defined by equation (*10*) is ideal. Now it will be useful to study the effects of gross deviations from the ideal condition. Consider a suspension which has been settling for a known interval of time under controlled conditions. Imagine a hydrometer lowered into this suspension and allowed to come to rest, with the bulb extending from the depth h_1 down to the depth h_2 (fig. 2b). Because the plane of average density must lie within the zone which controls the hydrometer reading (cross-hatched area in fig. 2a), the effective depth will be found between h_1 and $(h_1 + \frac{L}{\alpha})$. The size distributions which will be least favorable to accuracy will be those in which the plane of average density lies at one or the other of these two extremes. Therefore, regardless of the peculiarities which might be shown by individual size distributions, the extreme positions which could be occupied by the plane of average density will be definite. These depth values, when entered in Stokes' equation, will define the range of diameters within which the correct value of d is bound to lie. It will be convenient to use as a norm the value of d (now to be designated d_E) calculated from the theory of this article, and to record the extreme values as fractions of this amount. Thus, from equation (*13*) it will be found that

$$d_E = \sqrt{\frac{18\eta h_E}{gt(\sigma - \rho)}} \tag{15}$$

$$d_1 = d_E \sqrt{\frac{h_1}{h_E}} \tag{16}$$

$$d_2 = d_E \sqrt{\frac{h_1 + \frac{L}{\alpha}}{h_E}} \tag{17}$$

The extreme values for the diameter are plotted in figure 3. For convenience, the ordinates are calculated relative to the value of d_E, which places the values of d_e on a horizontal line intermediate between the two limiting values. This procedure is justified by the fact that under the ideal conditions previously described, d_E will represent the exact value of diameter sought.

The significance of the curves can be realized by considering a particular case. Suppose that in a given measurement the hydrometer sinks to a depth of 1.5 L, that is, $h_1/L = 1.5$, and that equation (*15*) gives a theoretical particle size (d_E) equal to 2.0 μ. By inspection of figure 3 it will be found that the correct diameter will lie within the following limits:

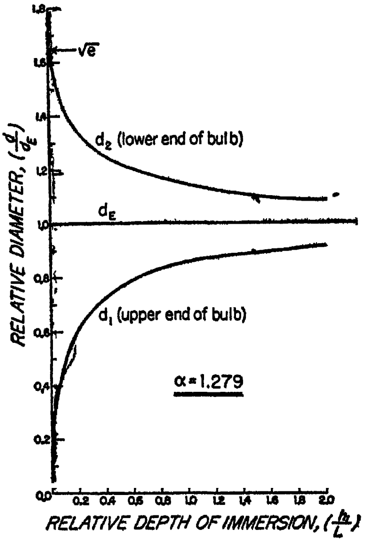

FIG. 3. CALCULATION OF PARTICLE SIZE; LIMITS OF VARIATION FROM CALCULATED DIAMETER FOR NON-IDEAL DISTRIBUTIONS

$$d_1 = 2.0 \times 0.89 = 1.8\ \mu$$

$$d_2 = 2.0 \times 1.1 = 2.2\ \mu$$

It will be seen in this case that an unfavorable size distribution could produce a maximum error of only 0.2 μ. In general, the maximum error from this cause would be represented in figure 3 by the vertical distance from the horizontal line to either of the limiting curves. That is, the correct value may lie anywhere between the two curves, whereas the calculated value represented by d_E will always lie almost midway between them.

The maximum error indicated in figure 3 could occur for certain types of particle size distributions, for example, in a nearly monodisperse system at the moment when the sharp boundary between concentrated suspension and clear liquid passes the depth h_1. At the given instant, the average concentration in the zone of measurement would be slightly less than the initial concentration, and the plane of average concentration would occur on the density boundary at h_1. The correct value for diameter, therefore, would be found on the lower curve instead of the middle one. Natural size distributions of this extreme type are rare.

The amount of error resulting from an unfavorable size distribution will be partly controlled by the depth of immersion of the hydrometer. In general, the more deeply the hydrometer sinks during the measurement, the less will be the magnitude of the error caused by assuming an ideal distribution. Figure 3 shows that the error increases sharply below h_1 0.5 L, and for this reason it is recommended that depths of immersion less than this value be avoided.

From the information provided by figure 3 it can be concluded that the effects of nonideal size distributions are predictable, within definite limits. In view of the fact that these limits represent the worst possible conditions for the application of the theory, one may usually expect very much more favorable results than indicated in the figure. Further evidence for this conclusion is produced in the following section.

APPLICABILITY OF THE METHOD

According to the theory of this article, accuracy will be affected if the soil under study does not conform to the ideal type of size distribution. It would be desirable, therefore, to have a means of judging the reliability of the theory in specific cases. Moreover, no limits have yet been set on the range of diameters within which the ideal distribution must hold in order to satisfy the theoretical requirements. These questions can now be answered.

As before, consider the situation represented in figure 2b. Because the rest point is affected only by that part of the suspension which contains the bulb, it is required that equation (*1*) be satisfied only between the depths h_1 and h_2. This requirement will be met, for given conditions of sedimentation, if the summation curve is linear between the diameters d_1 and d_2 calculated from Stokes' equation for the depths h_1 and h_2 respectively. It will be recognized that the curves in figure 3 contain the information necessary for determining these diameter limits. Thus, a vertical line drawn upon a particular value of h_1/L will intersect the curves at the desired values of d_1 and d_2.

The measurements will comply with the theoretical conditions if the summation curve is linear between the diameter limits shown in figure 3 for a given depth of immersion. If the summation curve is nonlinear in this interval, the amount of discrepancy between actual and theoretical values of diameter will depend upon the amount of deviation from linearity, but even in extreme cases the discrepancy will not be more than approximately half the width of the interval.

The interval between the two curves in figure 3 represents a rather narrow range of sizes. Ordinarily, any selected narrow section of a summation curve can be satisfactorily represented by a straight line segment; therefore it is reasonable to expect the present theory to be valid in the majority of cases.

COMPARISON OF THE PRESENT METHOD WITH PREVIOUS METHODS

The most complete theory of the hydrometer method hitherto available has been that of Casagrande. In Casagrande's theory, the center of volume of the hydrometer bulb was assumed to coincide with the plane of average density. A comparison of the present method with Casagrande's method is shown in figure 4. The two methods of calculating effective depth agree for deep immersion of the hydrometer, but differ by 36 per cent in the extreme case where $h_1/L = 0$. For the minimum depth of immersion recommended in this article, the discrepancy is only 5 per cent. Careful study of Casagrande's method shows that his choice of the center of volume as the plane of average density is equivalent to the assumption of a linear density gradient in the suspension. The sharp curvature of the density-depth function in the upper part of the suspension illustrated in figure 1 has the effect of placing the point of average density *above* the center of volume. Therefore the effective depth is actually less than predicted from Casagrande's equation, and the discrepancy becomes greatest at shallow depths of immersion where the density gradient is steepest.

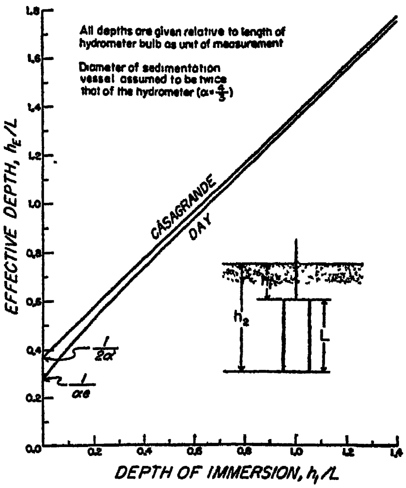

FIG. 4

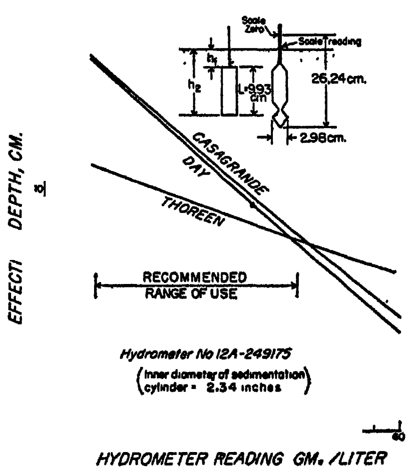

FIG. 5

FIG. 4. COMPARISON OF PRESENT THEORY WITH CASAGRANDE'S THEORY FOR VARIOUS DEPTHS OF IMMERSION

FIG. 5. DEPTH CALIBRATION OF A BOUYOUCOS HYDROMETER

The failure of the Casagrande method for shallow depths of immersion was previously shown by Codoni. Codoni proposed an alternative method which, although soundly based, had a limited range of usefulness because of inclusion of the parameters of distribution in his equation for effective depth.

For a number of years, the empirical method of Thoreen has been recommended as a standard method by the American Society for Testing Materials.[7] Figure

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[7] American Society for Testing Materials. Procedures for Testing Soils, pp. 19–29. ASTM, 1916 Race St., Philadelphia 3, 1944.

5 shows a calibration curve of a hydrometer of the type to which the Thoreen calibration was meant to apply. This is the original Bouyoucos design of hydrometer, designated as the type-A hydrometer by the ASTM. Although the bulb is not an exact cylinder, there is probably little error in theoretically replacing the actual bulb by a true cylinder of the same volume, provided that the centers of volume of the real and hypothetical bulbs are made to coincide. There is a large discrepancy between the Thoreen method and the other two methods illustrated. Although the agreement is good at a concentration of 40 gm. per liter, where the calibration curves cross, the deviation of the Thoreen value of effective depth from the one derived in the present article is about 30 per cent at low concentrations (deep immersion). Although Thoreen based his calibrations upon comparisons with the pipette method, the 0.42 factor which he obtained for computing effective depth from the depth of immersion of the tip varied widely among the different soil suspensions upon which the average factor was based. As no criteria were available as to whether a given suspension might conform closely or depart widely from the accepted figure, the Thoreen correction has never engendered great confidence in the results obtained through its use.

SUMMARY AND CONCLUSIONS

Determination of particle size by Stokes' equation requires accurate knowledge of the settling depth. Failure to fulfill this requirement has been a limitation of the hydrometer method. To remedy the defect, a new method of calibration has been developed, the physical basis of which is briefly described below.

In a particular soil suspension settling under gravity, the concentration of suspended soil at an arbitrary time after mixing was found to be a logarithmic function of depth. This result led to the idea that a logarithmic concentration gradient might be a general characteristic of soil suspensions undergoing sedimentation. The latter hypothesis was used in the development of the theory. It was shown that a cylindrical hydrometer placed in a suspension of the type just described would register the density of the suspension at a definite depth, which could be calculated from the depth of immersion of the hydrometer at the time of measurement, and from the dimensions of the hydrometer and sedimentation vessel. Moreover, it was shown that the effective depth was invariant with respect to the parameters in the concentration-depth function. Therefore a hydrometer calibration derived from this theory would give the effective depth as a function of the depth of immersion and would apply uniformly to all suspensions of the given type even though they might differ widely in concentration and in magnitude of concentration gradient.

It was found that the requirement of a logarithmic density gradient would be satisfied by any soil in which the particles were equally distributed, by weight, over a geometric progression of size intervals within a narrow range above and below the calculated size. This would make the new method most accurate for those sizes which occur on straight sections of the summation curve, when the latter is plotted on a logarithmic scale of sizes. More specifically, it was shown that for greatest accuracy the summation curve must be linear over a definite range of sizes, the limits of which can be determined as shown in figure 3. From a study of this figure, it was recommended that depths of immersion (h_1) shallower than half the length of the bulb be excluded from the working range of the hydrometer, for the range of linearity required in the summation curve would be less than ± 25 per cent of the measured size (± 0.1 cycle on the logarithmic scale).

It was shown that the particle size distributions which would be most unfavorable to the theory were uncommon, and that even the most extreme ones would affect the accuracy to a relatively minor degree, in an amount which could be predicted.

The new theory corrects the defect in the Casagrande theory and provides an expression for effective depth which is free of the limitations imposed in Codoni's theory. It offers an improvement over the empirical Thoreen calibration. The method requires a hydrometer having a cylindrical bulb, calibrated for use with a straight-sided sedimentation cylinder of known diameter. Calibration of hydrometers in accordance with the method described should enable the attainment of greater accuracy in hydrometer analysis than has been possible hitherto.

FIXATION OF AMMONIUM IN DIFFICULTLY EXCHANGEABLE FORM UNDER MOIST CONDITIONS BY SOME SOILS OF SEMIARID REGIONS[1]

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Received for publication April 11, 1950

In a recent study of some saline and alkali soils from the San Joaquin Valley of California, the Rubidoux unit of these Laboratories obtained analyses for a subsoil sample showing its degree of saturation with exchangeable Na to be over 40 per cent greater than its cation-exchange capacity as determined by the conventional neutral *N* ammonium acetate method. Investigation of this discrepancy has led to a study of NH_4 fixation under moist conditions by the aforementioned and other related soil samples. The literature on NH_4 fixation by soils was recently reviewed by Stanford and Pierre (5) and will be referred to herein only where pertinent. The purpose of this paper is to present data on (*a*) the amounts of NH_4 fixed by the various samples studied, (*b*) the effect of NH_4 fixation upon cation-exchange capacity, and (*c*) the relation of NH_4 fixation to K fixation.

MATERIALS AND METHODS

Soils studied

The soils studied, together with some data on their chemical characteristics, are given in table 1. All samples except 2650, 2654, and 2659, which are from land adjacent to the Salinity Laboratory, are from the San Joaquin Valley.

Fixation determinations

Fixation determinations were made under moist conditions only, because preliminary tests showed that alkaline soils could not be dried without loss of applied NH_4 through volatilization. In conducting fixation determinations, duplicate 5-gm. samples of soil were placed in 50-ml. centrifuge tubes. A 5-ml. aliquot of a solution containing the desired amount of NH_4Cl or KCl or of both was then added to one of the tubes. The remaining tube, which served as a control, received 5 ml. of distilled water. After a contact period of 24 hours at a temperature of 25 ± 3° C. the soil in both tubes was extracted with the desired salt solution or acid (6, p. 100), and the extracts were analyzed for the appropriate cation or cations. The amount of NH_4 or K fixed was obtained by subtracting the amount of the cation recovered upon extraction from the sum of that added and that removed from the control sample.

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[1] Contribution from the U.S. Regional Salinity and Rubidoux Laboratories, U.S. Department of Agriculture, Riverside, California, in cooperation with the eleven Western States and the Territory of Hawaii. The writer is indebted to the Staff of the Rubidoux unit of these Laboratories for some of the data given in table 1.

Analytical methods

All analytical methods except those for the determination of organic matter, Na, K, and cation-exchange capacity by Na are given in reference (6). Organic matter was estimated according to Peech *et al.* (3); Na and K were determined by means of a Perkin-Elmer model 52-A flame photometer, using Li as an internal standard. In determining cation-exchange capacity by Na, the soil sample was saturated with Na by treatment with neutral *N* sodium acetate solution. After removal of the excess sodium acetate by washing with 95 per cent ethanol, exchangeable Na was replaced with *N* ammonium acetate solution.

TABLE 1

Ammonium fixation and other chemical data for soils studied

SAMPLE NO.	SOIL TYPE	DEPTH	ORGANIC MATTER	pH OF SATURATED SOIL	EXCHANGEABLE Na	EXCHANGE CAPACITY BY NH_4	EC_e* AT 25°C.	NH_4 FIXED AGAINST 0.5 *N* KCl†
		in.	*per cent*		*me./100 gm.*	*me./100 gm.*	*millimhos/cm.*	*me./100 gm.*
R-3504	Traver fine sandy loam	0–5	1.21	7.0	1.9	8.5	14.3	0.0
R-3505		5–20	0.61	8.3‡	4.5	9.8	4.1	0.0
R-3506		20–34	0.28	8.7‡	5.7	7.9	4.3	0.6
R-3507		34–60	0.29	9.0‡	12.4	11.5	2.5	4.2
R-3510	Pachappa sandy loam	0– 6	0.71	7.1	0.3	6.3	0.6	0.0
R-3511		6–28	0.55	7.3	3.8	10.0	3.2	1.3
R-3512		28–60	0.38	8.5‡	7.2	9.5	6.0	1.7
R-3514	Pond loam	0– 4	1.50	7.7‡	6.8	18.8	8.5	0.2
R-3515		4–28	0.17	8.3‡	15.1	21.5	1.9	0.0
R-3516		28–60	0.21	8.4‡	17.6	25.3	1.2	1.8
R-3520	Madera sandy loam	0– 3	1.26	6.2	0.5	12.4	1.4	0.6
R-3521		3–12	0.62	7.3	2.4	12.9	2.5	1.1
R-3522		12–48	0.33	7.9‡	4.5	12.0	13.4	1.0
R-3524	Traver fine sandy loam	0– 9	0.71	8.4‡	9.8	17.2	2.2	0.0
R-3525		9–24	0.10	9.9‡	13.9	13.8	2.0	0.8
2647		25–60	0.04	10.0‡	10.9	7.4	2.5	3.5
R-3528	Chino loam	0–20	1.05	7.5‡	0.3	19.1	0.5	4.3
R-3529		20–60	0.22	7.6‡	0.3	19.9	0.4	6.2
2650	Pachappa fine sandy loam	11–13	0.22	7.7	0.2	10.0	0.3	3.0
2654		35–37	0.09	8.0	0.3	10.3	0.2	3.7
2659		65–67	0.04	8.1‡	0.6	10.6	0.4	4.9

* Symbol for electrical conductivity of saturation extract.

† NH_4 was applied as NH_4Cl at the rate of 10 me./100 gm.

‡ Indicates that sample is slightly calcareous.

RESULTS

Amounts of NH_4 fixed by various soils

As shown in table 1, the exchangeable Na content of soil sample 2647 greatly exceeds its cation-exchange capacity as determined by the neutral *N* ammonium acetate method. Inasmuch as the soil has a very high pH value, it was at first thought that possibly complete saturation of the soil exchange material and an accurate determination of exchange capacity could be obtained only by use of an ammonium acetate solution having a similar high pH value. However, results for exchange capacity obtained using ammonium acetate solutions adjusted to pH values of 8, 9, 10, and 11, by the addition of NH_4OH, did not differ significantly from that obtained at pH 7. In view of Stanford and Pierre's (5) recent work on NH_4 fixation under moist conditions by calcareous Iowa soils, attention was then given to the possibility that some of the NH_4 applied as ammonium acetate during the determination of exchange capacity was fixed in difficultly exchangeable form, thus causing a low value for capacity. To ascertain whether soil 2647 retains NH_4 in difficultly exchangeable form, fixation determinations involving applications of NH_4Cl at various rates were made. The results of these determinations, which are given graphically in figure 1, show

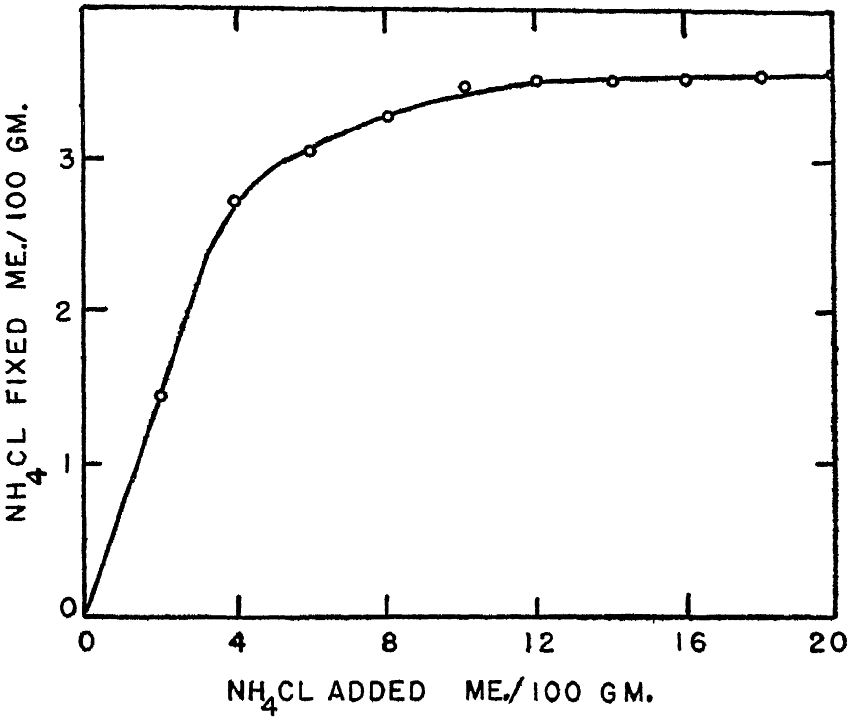

FIG. 1. FIXATION OF NH_4 BY SOIL 2647

that the soil has a high NH_4-fixation capacity. It will be noted that large fractions of the NH_4 applied at the two lower rates were fixed and that the fixation capacity was virtually satisfied when NH_4Cl was applied at the rate of 10 me. per 100 gm. of soil.

Data on the amounts of NH_4 fixed by other soil samples when an NH_4Cl application rate of 10 me. per 100 gm. was employed are included in table 1. Of the 21 soil samples studied, 15 fixed appreciable amounts of NH_4. In general, the amount of NH_4 fixation increases with depth in the soil profile but no clear-cut relation between NH_4 fixation and any of the other chemical data given in table 1 for the soil samples is evident. It will be noted that fixation by the surface layers is generally absent or very low.

In the preceding studies, the amount of applied NH_4 retained by the soil upon extraction with 0.5 *N* KCl was arbitrarily used as a measure of fixation. Because the K ion may also be fixed under moist conditions by soils of semiarid regions (2), it seemed advisable to determine the amounts of NH_4 fixed by several soils against extraction by a salt solution containing a cation such as Na, which is not known to undergo fixation. Comparisons of the amounts of NH_4 fixed against extraction by 0.5 *N* KCl and 0.5 *N* NaCl are given for eight soils in table 2. The data show that although the magnitudes of the amounts of NH_4 fixed in the two cases are similar, three of the eight soils fix slightly more NH_4 when 0.5 *N* KCl is employed as an extractant. These results indicate that possibly because of its smaller size the Na ion can replace NH_4 from some positions not accessible to the K ion.

TABLE 2

Comparisons of amounts of NH_4 fixed by various soils against extraction by 0.5 N *KCl and 0.5* N *NaCl*

SAMPLE NO.	NH_4 FIXED AGAINST		DIFFERENCE
	0.5 *N* KCl*	0.5 *N* NaCl*	
	me./100 gm.	*me./100 gm.*	*me./100 gm*
R-3504	0.0	0.0	0.0
R-3507	4.2	3.6	0.6
R-3510	0.0	0.0	0.0
R-3516	1.8	1.7	0.1
R-3520	0.6	0.0	0.6
R-3529	6.2	6.1	0.1
2647	3.5	3.4	0.1
2659	4.9	4.1	0.8
Ave.	2.65	2.36	

* NH_4 was applied as NH_4Cl at the rate of 10 me./100 gm.

Effect of NH_4 fixation upon cation-exchange capacity

The influence of NH_4 fixation upon cation-exchange capacity was studied by determining the capacity of eight soils to adsorb Na from neutral *N* sodium acetate solution before and after NH_4 fixation, the rate of NH_4Cl application being 10 me. per 100 gm. of soil. Table 3 gives the amounts of NH_4 fixed against extraction by *N* sodium acetate solution, the cation-exchange capacities by Na before and after fixation, and the reductions in exchange capacities due to NH_4 fixation. The data show that fixation of NH_4 by the soils causes reductions in their exchange capacities by amounts which are very nearly equal to the amounts of NH_4 fixed. The exchange capacities of four of the soil samples were reduced by more than 20 per cent by fixation of NH_4.

TABLE 3

Effect of NH_4 fixation upon cation-exchange capacities of various soils as determined by saturation with Na

SAMPLE NO.	CATION-EXCHANGE CAPACITY BY Na SATURATION		REDUCTION IN CAPACITY DUE TO NH_4 FIXATION		NH_4 FIXED AGAINST *N* SODIUM ACETATE
	Before NH_4 fixation	After NH_4 fixation*			
	me./100 gm.	*me./100 gm.*	*me /100 gm.*	*per cent*	*me./100 gm.*
R-3504	8.7	8.7	0.0	0.0	0.0
R-3507	15.6	12.2	3.4	21.8	3.6
R-3510	6.3	6.2	0.1	1.6	0.0
R-3516	27.2	25.4	1.8	6.6	1.8
R-3520	12.3	12.2	0.1	0.8	0.0
R-3529	26.6	20.7	5.9	22.2	6.1
2647	10.8	7.4	3.4	31.5	3.5
2659	15.8	12.0	3.8	24.0	4.1
Ave.	15.42	13.10	2.32	13.6	2.39

* NH_4 was applied as NH_4Cl at the rate of 10 me./100 gm.

TABLE 4

Comparisons of amounts of NH_4 and K fixed by various soils

SAMPLE NO.	NH_4 FIXED AGAINST 0.5 *N* KCl	K FIXED AGAINST 0.5 *N* NH_4Cl	DIFFERENCE
	me./100 gm	*me./100 gm.*	*me./100 gm.*
R-3504	0.0	0.6	0.6
R-3524	0.0	0.6	0.6
R-3525	0.8	1.6	0.8
R-3529	6.2	6.0	0.2
2647	3.5	3.4	0.1
2650	3.0	3.3	0.3
2654	3.7	3.8	0.1
2659	4.9	4.0	0.9
Ave................	2.76	2.91	—

In connection with these findings, it is pertinent to compare the differences in the cation-exchange capacities of the eight soils as determined by NH_4 (table 1) and by Na before fixation (table 3) with the amounts of NH_4 which they fix as given in table 1. These comparisons show that the differences in exchange capacities obtained with the two cations are similar to the amounts of NH_4 fixed.

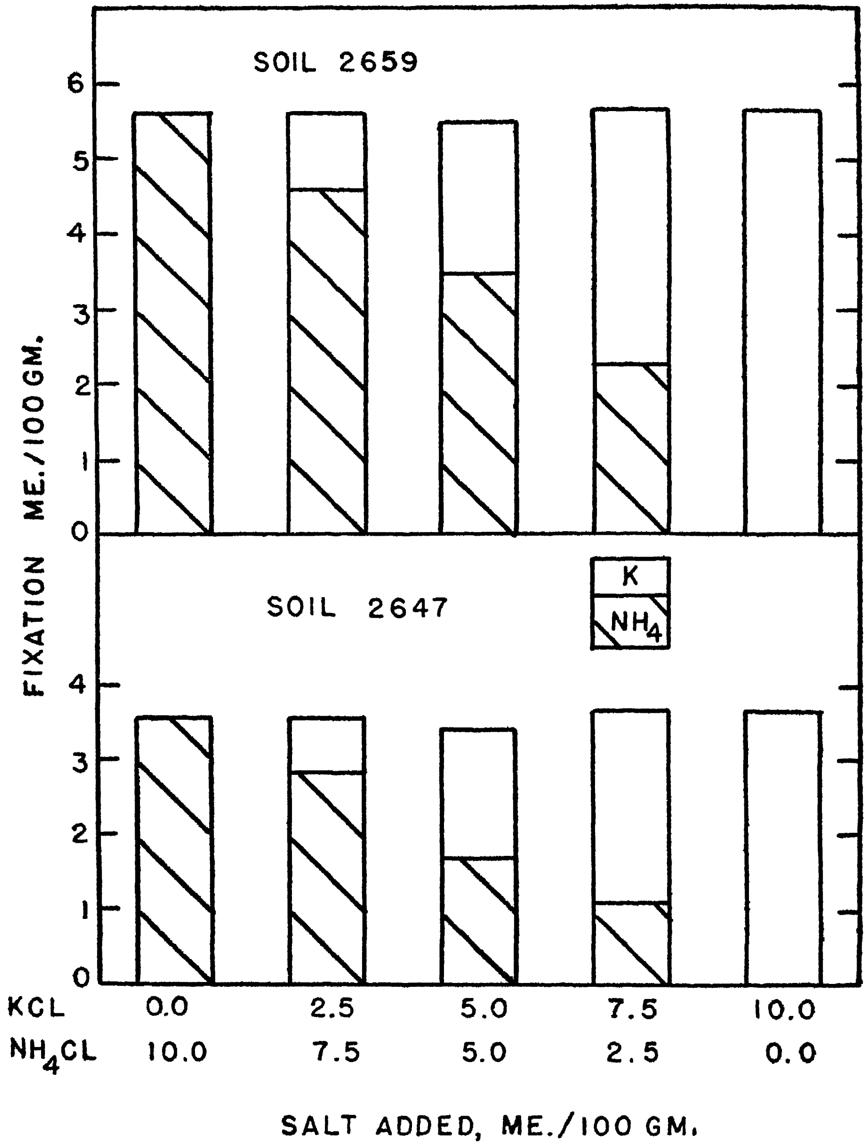

FIG. 2. RELATION BETWEEN NH_4 FIXATION AND K FIXATION

On the basis of the data presented in this section, it is apparent that the lower values for capacity obtained by the neutral *N* ammonium acetate method are largely, if not entirely, due to fixation of some of the applied NH_4 in difficultly exchangeable form.

Relation of NH_4 fixation to K fixation

Stanford and Pierre (5) found that NH_4 and K are fixed by the same mechanism under moist conditions by calcareous Iowa soils. It was, therefore, of interest to determine whether their finding holds for the soils under investigation. Preliminary data on this point were obtained by comparing the amounts of NH_4 and K fixed by various soil samples when NH_4Cl and KCl were applied at the rate of 10 me. per 100 gm. of soil. As shown in table 4, the agreement between the amounts of NH_4 and K fixed are sufficiently good to suggest strongly that the fixation mechanisms are essentially the same. More conclusive evidence in this regard was obtained by determining the amounts of NH_4 and K fixed by two soils against extraction by 0.2 *N* acetic acid when NH_4Cl and KCl were applied singly and as mixtures in various proportions. The results of these determinations, which are presented graphically in figure 2, show that the sums of the amounts of NH_4 and K fixed are practically the same for all fixation treatments. Sample 2659 appears to fix NH_4 selectively, whereas in sample 2647 no preference is apparent. Direct evidence that the addition of KCl causes a reduction in NH_4 fixation is obtained by comparing the amounts of NH_4 fixed by sample 2647 when NH_4Cl was applied at various rates alone (fig. 1) and in combination with KCl (fig. 2). For example, when NH_4Cl and KCl were applied together, each at the rate of 5 me. per 100 gm., only 1.7 me. of NH_4 per 100 gm. of soil was fixed as compared with a value of 2.9 me. per 100 gm. of soil obtained when the same amount of NH_4Cl was applied alone.

DISCUSSION

Probably the first studies on NH_4 fixation by soils were reported by McBeth (1) in 1917. This investigator found that under moist conditions some soils fixed applied NH_4 in a form such that it could not be removed by alkaline distillation or by extraction with 10 per cent HCl solution, that NH_4 fixation usually increased with soil depth, and that within the group of soils studied those from semiarid regions fixed much more NH_4 than those from humid regions. Moreover, he showed that the capacity of soils to fix NH_4 was greatly reduced by pretreatment with Al-, Fe^{+++}-, and K-salt solutions. Though knowledge regarding soil clays and cation exchange was insufficient in 1917 to enable McBeth to elucidate the nature of NH_4 fixation, his findings are noteworthy in light of the present work and that of Stanford (4) and Stanford and Pierre (5). In the present study the amounts of NH_4 found to be fixed at various depths by soils of semiarid regions are of the same magnitude as those reported by McBeth, and the data of Stanford and Pierre substantiate his finding regarding the relative amounts fixed under moist conditions by alkaline and by acid soils from humid areas. The work of Stanford and Pierre and that reported herein show that under moist conditions NH_4 and K are fixed by the same mechanism. McBeth's data showing that prior treatment of soil with K-salt solutions largely eliminates NH_4 fixation are in agreement with this finding.

On the basis of the present data showing that NH_4 fixation is accompanied by a corresponding reduction in cation-exchange capacity, it is apparent that the fixation process involves a cation-exchange reaction. According to Stanford (4) clay minerals of the illite (hydrous mica) type are responsible for the K fixation which occurs without drying. The fixation capacity under moist conditions for the illite which Stanford studied was about 1.5 me. per 100 gm. Obviously, the occurrence of illite of this fixation capacity in the present soils studied will not account for all of the NH_4 fixation observed. This means that many of the soils studied either contain hydrous mica having a very much higher fixation capacity under moist conditions than the above, or that possibly another variety of mineral is involved in the fixation process.

In his studies on K fixation, Stanford (4) found that the amount of fixation by illite increased markedly as the pH value was increased by the addition of NaOH or $Ca(OH)_2$. Furthermore, he presented data which indicated that treatment with hydroxide facilitates fixation by removing Al and Fe from positions where K normally becomes fixed. In view of the data showing that NH_4 and K are fixed by the same mechanism, Stanford's findings provide a probable explanation for the observed differences in amounts of NH_4 fixed by alkaline and acid soils and for McBeth's data showing that the prior addition of Al- and Fe^{+++}-salt solutions greatly decreases NH_4 fixation.

Information on NH_4 fixation by soils is of practical importance from at least two standpoints: First, as shown in this paper, the use of the neutral *N* ammonium acetate method for the determination of cation-exchange capacity gives low values when applied to soils that fix NH_4 under moist conditions, and second, it would seem highly probable that the ability of a soil to fix appreciable amounts of NH_4 will influence its nitrogen economy. Several of the subsoil layers studied are capable of fixing more than 2,000 pounds of NH_4-N per acre foot.

SUMMARY

Studies involving determinations of the amounts of NH_4 fixed under moist conditions, the effect of NH_4 fixation upon cation-exchange capacity, and the relation of NH_4 fixation to K fixation were made on a group of soil samples from semiarid regions. When NH_4Cl was applied at the rate of 10 me. per 100 gm. of soil, the amounts of NH_4 fixed by various samples against extraction by 0.5 *N* KCl ranged from 0.0 to 6.2 me. per 100 gm. Of the 21 samples studied, 15 fixed appreciable amounts of NH_4. By comparing the amounts of NH_4 and K fixed under similar conditions, and by studying the influence of K additions upon NH_4 fixation, it was concluded that under moist conditions the soils studied fix these cations by essentially the same mechanism. Results were presented showing that fixation of NH_4 causes a corresponding reduction in cation-exchange capacity and that the neutral *N* ammonium acetate method for the determination of cation-exchange capacity gives low values when applied to soils which fix NH_4 under moist conditions.

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EFFECT OF PAST MANAGEMENT AND EROSION OF SOIL ON FERTILIZER EFFICIENCY[1]

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Received for publication April 17, 1950

Sheet erosion is an indication of the kind of management that leads to soil deterioration even on level land. If the land is sloping and exposed to the impact of raindrops, sheet erosion may start. This tends to be a selective process on many soils. Not only are the fine particles of surface litter removed, but there is a natural tendency for the finer soil particles that are relatively high in organic matter and plant nutrients to be removed (4, 5, 6). It has also been shown that the material removed has a high concentration of soil microflora (9).

Plots were available in New York that had been used to study erosion on four soils for periods up to 11 years. Results of the first phase of the study, namely, measurement of erosion losses under various management and cropping practices, have been reported (1, 3). This paper is concerned with the second phase of the work—the extent of erosion damage as reflected in yields under uniform cropping and management. It will be shown that the productive capacity of these soils is related to the degree of past erosion even though chemical nutrients are present in ample supply.

PROCEDURE AND RESULTS

High-lime till soil

The Soil Conservation Station near Marcellus, New York, is on Honeoye gravelly silt loam at an elevation of approximately 1,000 feet. In 1939, plots to measure runoff and erosion under extremes of cover were installed on an 18 per cent west slope. These were 21 feet wide and 72.6 feet long with a minimum of 12 feet between plots. Two were kept fallow from 1939 to 1943, and two adjacent plots were in alfalfa-grass meadow for the same period. The fallow plots lost 270 tons of soil per acre or approximately 2 inches in 4 years (table 1). The meadow plots lost 1.4 tons.

In 1943, 8 tons of farm manure and 150 pounds of 20 per cent superphosphate were plowed down on all plots and corn was planted. An excess of seed was planted, and the resulting stands were thinned to 16,000 plants per acre.

The eroded ex-fallow plots in 1943 produced 47 per cent as much corn silage as the ex-meadow plots (table 1). After the plots were cropped 4 years to corn, oats, and 2 years of an alfalfa mixture, the corn crop on the eroded plots in 1947 was only about 70 per cent of that on the ex-meadow plots. The subsoil at 18 inches contained carbonate limestone, and there was a good stand of alfalfa on all plots.

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[1] Contribution from the Division of Research, Soil Conservation Service, U.S. Department of Agriculture, in cooperation with Cornell University Agricultural Experiment Station.

In 1948, all plots were fertilized with 1,000 pounds of 10–10–10 per acre before the corn was planted. Damage to soil productivity was still evident in the crop yields for that year.

TABLE 1

Effect of past management and erosion on crop yields at Marcellus, New York

SOIL MANAGEMENT 1939–1942	TOTAL SOIL LOSS 1939–1942	CROP AND YIELDS PER ACRE*						SOIL ORGANIC MATTER	
		Corn 1943	Oats 1944	Mixed hay		Corn		Spring 1943	Fall 1946
				1945	1946	1947	1948		
	T./A.	*lb.*	*bu.*	*lb.*	*lb.*	*bu.*	*bu.*	*per cent*	*per cent*
Meadow	1.4	5700†	31	2920	4530	69‡	62‡	2.6	2.6
Fallow	270.0	2670†	21	2680	3900	49‡	52‡	2.0	2.2
Fallow plot yields as per cent of meadow		47	68	92	86	71	84		

* Farm manure at 8 tons per acre before corn in 1943 and 1947; 1,000 pounds 10–10–10 per acre plowed under for corn in 1948; 150 pounds 0–20–0 per acre for corn and 300 pounds 0–20–0 with oats.

† Dry matter. No grain yield in 1943, as corn did not mature.

‡ Bushels of shelled corn per acre, calculated on basis of 15 per cent moisture.

TABLE 2

Rainfall during growing season

STATION AND YEARS	MAY	JUNE	JULY	AUG.	SEPT.	TOTAL
	in.	*in.*	*in.*	*in.*	*in.*	*in.*
Arnot:						
Average 1935–1947	4.8	4.2	3.8	4.1	3.8	20.7
1946, actual	8.1	3.2	5.9	3.2	4.5	24.9
1947, actual	7.6	5.4	5.1	4.5	2.7	25.3
1948, actual	3.4	4.5	5.0	3.7	2.0	18.6
Geneva:						
Average from Weather Bureau records	3.0	3.4	3.3	2.8	2.8	15.3
1947, actual	5.3	2.8	3.7	5.8	2.4	20.0
1948, actual	5.1	3.5	1.5	3.1	1.7	14.9
Marcellus:						
Average 1937–1948	3.6	3.9	3.4	2.6	3.1	16.6
1943, actual	4.4	3.7	2.0	3.4	0.6	14.1
1944, actual	3.1	5.6	1.5	2.2	2.9	15.3
1945, actual	3.4	4.2	4.2	2.4	5.9	20.1
1946, actual	2.9	3.2	4.5	3.0	3.9	17.5
1947, actual	6.9	4.1	8.3	1.9	2.8	24.0
1948, actual	4.4	4.5	1.5	3.8	1.7	15.9

Rainfall data for the growing season at all sites are given in table 2. The data for Marcellus show no marked deficiencies during critical months for corn with the possible exception of July 1948.

High-elevation acid sandstone and shale till soil

The Arnot Soil Conservation Station is 17 miles southwest of Ithaca. In 1934–1935, plots to measure soil and water runoff were started on a 20 per cent east slope at an elevation of approximately 1,900 feet. The plots were 6 feet wide and those concerned in this report were 72.6 feet long. They were separated by 2-foot borders and bounded by steel plates 18 inches wide which projected 6 inches above the soil. The plots were spaded rather than plowed and were cultivated with hand tools.

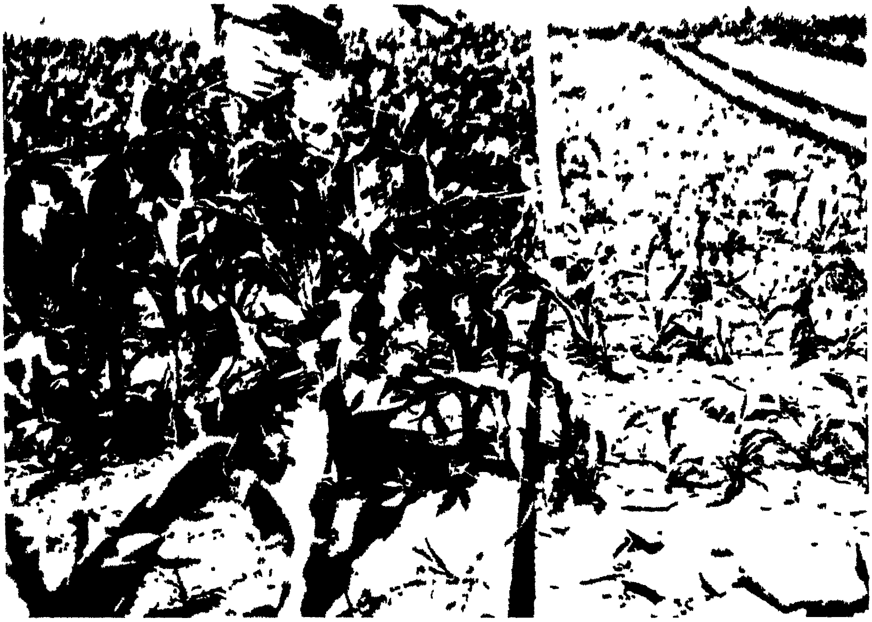

FIG. 1 EFFECT OF PREVIOUS MANAGEMENT AND EROSION ON CORN GROWTH AT ARNOT

Photograph taken July 1946. The plot at left had been in fertilized meadow from 1935 to 1945 and lost only a trace of soil by erosion. The plot at right had been fallow and lost 74 tons per acre. Both plots were heavily fertilized in 1946.

The soil is well drained and is similar to Lordstown flaggy silt loam except that it is deeper. It has a friable structure throughout the A and B horizons. The dilution of the topsoil with subsoil as erosion occurs would be expected to have little effect on structure and plant growth where mineral plant nutrients were supplied. Before the experiment was started in 1935, the area had been in a uniform cropping system of corn, oats, followed by 3 years of red and alsike clover with timothy hay. The soil management program included farm manure with limestone and superphosphate.

During the 11 years of runoff studies, the total soil loss varied, with the treatments, from a trace to 138 tons per acre. This was all due to sheet erosion. Approximately 95 per cent of the soil washed off was fine enough to pass through a 2-mm. screen. Only 29 per cent of the plow layer remaining will pass through the same screen.

In the spring of 1946, enough hydrated lime was applied to bring the soil reaction to pH 5.8. To each of the runoff plots, 1,000 pounds of 10–10–10 was applied and spaded in to plow depth. Both fertilizer and lime were worked through the plow layer in the process. Corn was planted on May 28. An excess of seed was used, and the stand was later thinned to 20,000 plants per acre.

The growth of corn was affected from the first by the degree of recent erosion, as shown by high germination where less soil had been lost. There was little evidence that the corn sprouts had difficulty penetrating the slight surface crust where the greatest soil losses had occurred. Yet, the corn plants were stunted on the eroded plots (fig. 1). Early in the season they showed clearly a lack of phosphorus and possibly other nutrient deficiencies. The root system on the eroded plots was restricted to a small volume of fairly dry soil. The soil between the plants was moist but contained few roots. On the better plots, the corn was large and green with a maze of roots throughout the soil surface layer.

TABLE 3

Effect of past management and erosion on yield of corn at Arnot Station, near Ithaca, New York

SOIL MANAGEMENT 1935–1945	TOTAL SOIL LOSS 1935–1945	CORN YIELDS PER ACRE*		RELATED SOIL FACTORS 1946	
		1946	1947	Organic matter	Degree aggregation
	T/A.	*bu*	*bu*	*per cent*	*per cent*
Idle	2	82	75	4.6	86
Meadow fertilized†	0	88	64	4.5	83
Rotation potatoes-sweet clover‡	13	57	63	4.1	75
Rotation corn-oats-clover (fertilized)§	3	64	47	4.7	79
Rotation corn-oats-clover (unfertilized)	8	38	42	3.8	80
Corn continuous (fertilized)¶	34	35	25	3.1	67
Corn continuous (unfertilized)	48	33	17	3.0	68
Fallow, stones in place	74	19	35	3.0	67
Fallow, stones removed‖	138	24	26	2.9	61

* Bushels per acre of shelled corn calculated on basis of 15 per cent moisture.

† Farm manure at 6 tons per acre and 16 per cent superphosphate at 600 pounds per acre every 3 years Limestone sufficient to grow clover

‡ Twelve hundred pounds 5-10-5 before potatoes.

§ Farm manure 6 tons before corn; limestone sufficient to grow clover; 300 pounds 0–16–0 before corn and also before oats.

¶ Two hundred pounds 5–10–5

‖ Stones above 2 inches any dimension removed.

Soil tests were made before fertilizer application and again just before the crop was harvested. The tests included organic matter, pH, phosphorus, both nitrate and ammonia nitrogen, calcium, magnesium, potassium, manganese, iron and aluminum.[2] The eroded plots were short of nutrients before the fertilizers were applied, but all nutrients were considered adequate after the uniform application of 1,000 pounds of 10–10–10, even at the latter part of the growing season. The high-yielding corn plots were generally higher in organic matter, pH, and phosphorus, and lower in manganese, iron and aluminum.

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[2] Soil tests through the cooperation of Michael Peech, Cornell University.

The organic matter and water-stable aggregates were definitely higher on those plots that had lost little topsoil (table 3). The organic matter was determined by the Wakley-Black method (8). The values so obtained were corrected by multiplying by a factor which was a ratio between the results obtained by this method and those by the customary method for determining organic carbon in the tube furnace by burning in pure oxygen. To establish the factor, at least one sample in ten was run by both methods. The degree of aggregation was determined from the formula $100 - (D - I)/D$, where D is the percentage of fines (particles passing 0.2-mm. sieve) in a mechanical analysis and I is the percentage of fines determined by wet aggregate analysis (10).

A compaction test (2) indicated that soil from the meadow plot reached a maximum compaction of 1.5 volume weight at 26 per cent moisture, whereas soil from the fallow plot reached that condition at a volume weight of 1.6 at 22 per cent moisture. The compactive force used was equivalent to that of a two-plow, rubber-tired tractor.

In 1947, the 10–10–10 fertilizer was applied in the same manner and rate as in the previous year, and corn was planted on June 5. Because of heavy rains in June and early July (table 2), 100 pounds of ammonium sulfate per acre was applied to all plots in mid-July. The corn exhibited much the same growth behavior as during the previous year. The plot that had been fallow with stones in place showed some improvement in yield, while the plot that had been in continuous corn seemed to deteriorate still further. Soil tests again indicated no nutrient deficiency. Rainfall appeared adequate during both 1946 and 1947, and even excessive during the latter year.

Mixed limestone till and glacial lake soils

The soils used for erosion-control experiments at Geneva are Ontario sandy clay loam and Dunkirk silty clay loam. The former is a limestone till soil, more deeply weathered than the Honeoye at Marcellus. The Dunkirk was laid down in glacial lake water and is still alkaline in the subsoil. The soil where the plots are situated had been subjected to severe sheet erosion before the experiments were started. The Ontario plots are on an 8 per cent slope facing north and the Dunkirk on a 5 per cent slope facing south. Plots on both soils are 6 feet wide and 72.6 feet long with 12 or more feet between plots. Both sets of plots have an elevation of approximately 600 feet.

Runoff measurements from orchard covers were started in 1936 and treatments were continued through 1946. The total soil loss from the continuous fallow plots on Ontario soil was 200 tons per acre for the period compared to a trace from bluegrass sod and intermediate amounts from the other treatments (table 4). The fallow plot on Dunkirk soil lost 352 tons per acre.

In 1947, 1,000 pounds of 10–10–10 was used—800 pounds turned under and 200 pounds applied in bands—on each plot of both series. Corn was planted on

June 7. An excess of seed was used, and the plants were thinned later to 20,000 per acre. The yields of corn varied from 62 to more than 100 bushels per acre on the Ontario plots and from 54 to 82 on the Dunkirk plots.

The fertilizing and planting procedures were the same in 1948 as in 1947. On the Dunkirk plots, the corn failed to emerge to a satisfactory stand in 1948 because of severe crusting on both plots. Cabbage was set out on these plots to replace the corn. It survived a summer drought and was stimulated to a fair yield on all plots by fall rains.

Sheet erosion here is not so selective a process as at Marcellus and at Arnot (6). The Ontario plots were a part of an orchard soil-management experiment with no crops removed. The vegetable crop rotation on the Dunkirk soil consisted of sweet corn, cabbage, beans, and wheat, with all crops removed. Winter cover crops were used. Here, as at the other locations, high erosion losses were associated with low organic matter, low degree of aggregation, low early growth rate, and relatively low yields of corn. In 1947 conditions for seedbed preparation were better at Geneva than at Marcellus and at Arnot because of a relatively low rainfall in June (table 2), but the early growth was slow on the seriously eroded plots (table 4). Later, with a very favorable August rainfall—5.8 inches—the growth rate became more uniform.

TABLE 4

Effect of past management and erosion on yield and rate of growth of corn at Geneva, New York

MANAGEMENT 1936–1946	TOTAL SOIL LOSS 1936–1946	CORN				RELATED SOIL FACTORS 1946	
		Yield per acre*		Growth per day 1947		Organic matter	Degree aggregation
		1947	1948	July 11–21	July 29–Aug. 11		
	T./A.	*bu.*	*bu.*	*in.*	*in.*	*per cent*	*per cent*
Ontario soil:†							
Bluegrass sod	Trace	100.4	93.1	2.2	3.2	2.4	55
Buckwheat sown in trash	9	97.2	105.8	2.2	3.2	2.4	60
Soybeans fall-plowed	7	94.9	81.6	2.1	2.9	2.1	40
Soybeans sown in trash	11	94.3	96.1	2.3	3.5	2.1	54
Winter rye, summer fallow	77	72.5	67.5	1.3	3.1	1.7	27
Continuous fallow	200	62.2	40.3	1.3	2.8	1.3	16
Dunkirk soil:‡							
Vegetable crop rotation	31	82.1	14.8§	1.1	3.2	1.7	—
Fallow	352	53.9	14.9§	0.4	2.1	1.1	—

* Bushels per acre of shelled corn calculated on basis of 15 per cent moisture.

† Ontario sandy clay loam; 2.0 per cent organic matter, 1936.

‡ Dunkirk silty clay loam. Rotation of corn, cabbage, beans, and wheat with applications of 5–10–5 at rate of 200 pounds per acre each year.

§ Cabbage, tons per acre (see text).

DISCUSSION

Previous studies (7) of the effect on crop yield of the depth of topsoil as a result of differential erosion have yielded valuable data. In this study, the erosion has been recent and the detailed progress recorded. The soil loss has been due to the impact of raindrops on exposed soil and to transportation of the detached particles for a short distance by thin sheets of water. Depth of topsoil is less important here than the selective removal of certain parts of the soil and the effect that this removal and soil exposure and cropping have had on the soil. Application of liberal amounts of mineral fertilizers failed to erase the effects of past management and the resulting differences in erosion. It may be well to emphasize that the row crops in all these experiments were planted across the slope. Losses of soil and water undoubtedly would have been greater in all cases had not this elementary control measure been followed.

The damage to the various soils, as expressed in reduced crop yields, varied and was not in direct proportion to the amount of soil washed off. The restricted growth of corn shown by small top and root growth indicates that the plant nutrients and water in the soil were used inefficiently. The greater corn yields on the less eroded plots were due to earlier maturity, size of ear and stalk, and fewer barren stalks, rather than to differences in stand, since the plots in each experiment were thinned to uniform stands. The early maturity was especially important in 1947, when a killing freeze occurred at all three locations on September 23.

Reduced aggregation and organic matter and increased compaction indicated that ready movement of water and air was restricted. Waste products of plant growth slough off or may be exuded from the growing root. This is energy material that stimulates the growth of soil organisms which use a large amount of oxygen. The partial exhaustion of oxygen may result in piling up of the waste products of the soil organisms and plants to a degree that is unfavorable to the growth of the latter. This may well be expressed as a poor condition of soil sanitation.

In the soil at the Arnot Station, more than two thirds of the plow layer consists of flaggy-shaped, fine-grained sandstone fragments. These range from 2 mm. to more than 8 inches in longest dimension. The silt loam soil fills the voids between the coarser materials. Obviously, a soil structure favorable to the ready movement of air and water is very important. There is some soil mottling on top of the larger flat rocks in a horizontal position. This indicates local restrictions in air movement.

It is difficult to separate the effects of past cropping and cultural practices from the effect of soil removal by erosion. Since one is the result of the other, perhaps such distinction is not essential. In the Honeoye soil, a large soil loss occurred in 4 years, a relatively short time. More of the damage there might be ascribed to erosion. Considerable recovery was made by applying farm manure and growing alfalfa-timothy hay, but the damage is still appreciable. The rate of recovery from erosion damage will probably vary with the nature of the soil. This third phase of the work, started in 1948 at Arnot and in 1949 at Geneva, is under way.

SUMMARY

Cropping and cultural practices that result in sheet erosion on the four soils studied rapidly led to reduced corn yields and inefficient use of fertilizer. Corn

fertilized with 1,000 pounds of 10–10–10 fertilizer on one soil varied from 17 to 88 bushels per acre; on another, from 40 to 106 bushels; and on still another, from 54 to 82 bushels. On the Honeoye soil, even after 2 years of alfalfa-clover-timothy hay, the yield of corn varied from 49 to 69 bushels per acre. These variations on all four soils were consistently related to the amount of erosion that had been measured during the period prior to the evaluation of erosion damage by uniform cropping to corn.

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CAUSES OF POOR GROWTH OF PLANTS ON ACID SOILS AND BENEFICIAL EFFECTS OF LIMING: I. EVALUATION OF FACTORS RESPONSIBLE FOR ACID-SOIL INJURY[1]

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Received for publication April 7, 1950

The use of liming materials to improve crop growth on acid soils has been the subject of extensive investigations; yet there is little agreement today as to the fundamental causes of the poor growth of plants on acid soils. The poor plant growth associated with acid soils is a complex function of many contributing factors, all of which may be modified by liming. Not until the relative importance of the different beneficial effects of liming acid soils is fully evaluated will it be possible to make the most intelligent use of lime.

The beneficial effect of liming was attributed by earlier investigators primarily to neutralization of soil acidity, but there has been considerable criticism of this theory (3, 36). Aside from possible direct toxicity of the H ion (7, 8, 13, 14), high H-ion concentrations have been shown to reduce the uptake of certain metal ions. Arnon, Fratzke, and Johnson (6) found that an increasing H-ion concentration in nutrient solutions decreased the uptake of Ca but had little influence on the absorption of K, Mg, and NO_3 ions by tomato and lettuce plants during short-time experiments. DeTurk (15) reported that red clover failed to grow at pH 5.0 in sand cultures containing 160 ppm. Ca but grew normally at pH 7.0 at the same Ca level. Experiments with soils to determine the influence of soil reaction on crop growth are complicated by many ecological factors that are associated with soil acidity, but it would appear that absorption of Ca by plants in acid soils may be restricted under conditions of extreme acidity.

Albrecht and co-workers (1, 3, 24) used the technique of growing soybeans in clay-sand cultures in their studies of the ecological factors associated with soil acidity. They concluded that the principal benefit from liming acid soils comes from Ca as a nutrient for the plants. It should be pointed out, however, that the amount of exchangeable Ca used in their sand-clay cultures was only one tenth to one twentieth that found even in many strongly acid soils. Allaway (5) and Mehlich and co-workers (33, 34, 35) found that plants could remove exchangeable Ca more readily from kaolinite than from montmorillonitic clays, but in this study the influence of several possible contributing factors, for example pH and soluble Al and Fe, cannot be fully evaluated, and therefore the differences observed do not necessarily reflect the true availability of Ca in the different clays. These same workers reported that the availability of Ca increased with the increasing degree of Ca saturation of the clay. Here again the soil reaction was also a variable, and consequently the uptake of Ca by the plants may have been influenced not only by the degree of Ca saturation but also by the H-ion concentration and the amount of readily soluble Al and Fe. If the principal beneficial effect of liming is due to the supply of the nutrient Ca, then soluble sources of Ca should be as satisfactory as limestone (4). Field trials (19, 20, 29, 38, 39) and the more recent greenhouse studies of Fried and Peech (17) have shown conclusively that gypsum, in contrast to lime, fails to improve plant growth on acid soils, and moreover, the use of soluble Ca salts on some soils may result in a decrease in yield (12, 25, 26). One exception is the effective use of gypsum in the production of peanuts on acid soils (45). The peanut fruit is apparently unable to absorb Ca from the soil unless there is a high Ca-ion concentration in the soil solution. This plant, however, is unique inasmuch as most of the Ca in the fruit is taken up directly from the soil and not through the main root system of the plant (10).

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[1] Contribution from the department of agronomy, Cornell University, Ithaca, N. Y. Part of a thesis submitted to the Graduate School by the senior author (National Lime Association Fellow; now at Colorado A. & M.) in partial fulfillment of the requirements for the degree of doctor of philosophy.

The solubility of Al, Mn, and Fe in the soil is markedly influenced by soil acidity. Several investigators have attributed the poor growth of plants in acid soils to the presence of toxic quantities of Al, Mn, or Fe in the soil. Fried and Peech (17) found that treatments that increased the concentration of Mn ions in the soil solution reduced the yield of alfalfa and increased the Mn content of the plants. Sherman and Fujimoto (46) obtained increased yields of carrots and lettuce with either a paper mulch or applications of $Ca(OH)_2$; both treatments decreased the exchangeable Mn in the soil. Kipps (25) reported that alfalfa yields were reduced and the plants became chlorotic when the Ca/Mn ratio in the plant was less than 66. Hewitt *et al.* (22, 51) have attempted to evaluate the significance of Mn toxicity as a factor responsible for the poor growth of plants on acid soils of England. They found that typical foliar symptoms observed on cauliflower and runner beans grown in acid soils could be produced on plants grown in sand cultures supplied with 12 to 25 ppm. Mn. The injury caused by excessive amounts of Mn could be alleviated by increasing the Ca-ion concentration in the culture solution. These workers have suggested that lime serves two functions when added to an acid soil: first it decreases the soluble Mn in the soil; and second, it provides a better Ca-Mn balance in the soil.

Ligon and Pierre (28), Wright (52), and others (12, 21, 44) have reported toxic concentrations of Al in many acid soils. Plant injury from excessive soluble Al in the soils could be reduced by any soil treatment which decreased the solubility of the Al. The addition of lime was found to be most effective, but the injury due to excessive amounts of soluble Al also could be prevented by liberal applications of phosphate (21, 43, 52), organic matter (21), and basic fertilizers (9). There is considerable doubt as to the cause of Al toxicity. Trenel and Alten (50) concluded that Al may be a root poison. Pierre and Stuart (43) and Wright (52) attributed the poor growth, at least in part, to root inujry. On the other hand, other investigators have suggested that plants grown in acid soils high in readily soluble Al may suffer from P starvation caused by precipitation of aluminum phosphate in the soil (30, 31, 32) or in the plant roots (22, 53). Trenel and Frey (48) and others (18, 26) reported that high concentrations of Al may reduce Ca uptake by the plant.

Although the literature has shown that the crop response to liming is due to a complex interaction of numerous factors, most emphasis has been placed on the soil-plant Ca relationships. The objective of this investigation was to study Ca level, soil reaction, Al, Mn, and Fe as factors causing the poor growth of crops, especially legumes, on Mardin silt loam. Emphasis has been placed on evaluation of the relative significance of the increased supply of Ca as a nutrient in determining the growth response of alfalfa to application of lime on this soil. This is a strongly acid, moderately well drained brown podzolic soil derived from glacial till composed of acid Devonian sandstone and shale. Legumes and certain cereals have been found to respond well to application of lime on this soil.

EXPERIMENT I

In experiment I three different experimental approaches were used to evaluate the significance of Ca supply as a factor contributing to the poor growth of plants on acid Mardin silt loam: first, the total Ca supply in the soli was varied at pH

4.75, 5.5, and 6.5 by diluting the soil with sand; second, gypsum was added to the soil at widely varying Ca levels; third, peat-sand cultures were used to study plant growth in an acid soil free of toxic concentrations of Al, Mn, or Fe. In conjunction with the main objective, the toxicity of Mn was studied by adding Mn to several treatments at varying levels of Ca.

Materials and methods

Alfalfa was grown in the green house in 1-gallon glazed pots containing either Mardin silt loam from the A_p horizon or peat-sand mixtures. Before treatment, the Mardin soil contained 15 pounds of Mg, 110 pounds of K, 55 pounds of Mn, 60 pounds of Fe, 400 pounds of Al, and 2 pounds P per 2,000,000 pounds soil, as determined by the rapid microchemical soil tests described by Peech and English (40). The unlimed Mardin soil contained 600 pounds exchangeable Ca per 2,000,000 pounds and had an exchange capacity of 14.0 me. per 100 gm. The pH of the soil was 4.75. The woody peat used in the experiment came from a farm near Rose, New York.

The soil was limed with $CaCO_3$ at rates determined from a titration curve prepared by the method of Bradfield and Allison (11) to give approximately pH 5.5 and 6.5. The soil at each reaction was mixed with varying amounts of quartz sand to reduce the exchangeable Ca content to very low levels, and gypsum was added to each of the soil-sand mixtures. Manganese was included in several treatments at low Ca levels. The peat was mixed with sand to provide an acid medium low in exchangeable Ca and also low in readily soluble Al, Mn, and Fe. The treatments are listed in table 1.

The peat used in the last four treatments was first leached with 0.5 *N* HCl to remove exchangeable bases and readily soluble Al, Mn, and Fe, and finally washed with water until free of chlorides. Sufficient $CaCO_3$ was added to the leached acid peat to give pH 4.8 or pH 6.5, and the peat was thoroughly mixed with quartz sand in amounts required to give the equivalent of 500 and 4,000 pounds Ca at pH 4.8 and 500 pounds Ca at pH 6.5 per 2,000,000 pounds of peat-sand mixture. All treatments with peat included 5 pounds Mn as $MnCO_3$, 2 pounds Cu as $CuSO_4 \cdot 5H_2O$, and 2 pounds Zn as $ZnSO_4 \cdot 6H_2O$ per 2,000,000 pounds peat-sand mixture.

Four thousand grams soil, or an equivalent volume of soil or peat plus sand was weighed out per pot. As a basal treatment, 200 pounds P_2O_5 as $NH_4H_2PO_4$ 85 pounds N as $NH_4H_2PO_4$ and KNO_3, 200 pounds K as KNO_3 and K_2SO_4, 100 pounds Mg as $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, 30 pounds S as K_2SO_4, and 25 pounds $Na_2B_4O_7 \cdot 10H_2O$ per 2,000,000 pounds soil were added to all pots.

Gypsum was added at the rate of 2 tons per 2,000,000 pounds of soil. This amount was sufficient to give a saturated solution at 30 per cent soil moisture content. In the Mn treatments, 100 pounds Mn per 2,000,000 pounds of soil was added as $MnCO_3$.

The soil and the added materials were thoroughly mixed in an end-over-end churn; treatments 1 to 24 inclusive were potted February 17, 1947, but the $MnCO_3$ was not added until March 17. Distilled water was added on the basis

TABLE 1

Plan of experiment I, and yield and chemical composition of alfalfa as affected by different treatments

NUMBER	TREATMENT*	VOLUME RATIO SOIL: SAND	pH AT END OF EXPERIMENT	EXCHANGEABLE Ca PER 2,000,000 LB. SOIL†	YIELD OF ALFALFA PER POT‡		CHEMICAL COMPOSITION OF ALFALFA					
							First cutting		Second cutting			
					First cutting	Second cutting	Ca	Mn	Ca	Mn	P	N
				lb.	*gm.*	*gm.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	Soil pH 4.75, control	1:0	4.60	600	0.64	1.45	0.86	0.041	1.60	0.073	0.31	5.41
2	Soil pH 4.75 + gypsum	1:0	4.35	600	1.13	2.06	1.02	0.048	1.80	0.077	0.31	5.16
3	Soil pH 4.75 + sand	1:1	4.85	300	2.39	4.29	1.62	0.041	1.19	0.025	0.27	3.73
4	Soil pH 4.75 + sand + gypsum	1:1	4.35	300	1.44	2.74	1.09	0.050	1.90	0.017	0.31	5.32
5	Soil pH 4.75 + sand	1:3	5.10	150	3.52	4.77	1.29	0.027	0.72	0.010	0.27	3.09
6	Soil pH 4.75 + sand + Mn	1:3	5.10	150	1.46	2.72	0.72	0.066	0.79	0.040	0.28	3.76
7	Soil pH 4.75 + sand + gypsum	1:3	4.50	150	3.34	4.38	2.14	0.067	1.58	0.040	0.28	3.04
8	Soil pH 4.75 + sand + Mn + gypsum	1:3	4.50	150	0.88	1.16	0.99	0.129	1.85	0.228	0.22	4.80
11	Soil pH 5.5	1:0	5.45	2100	5.68	7.16	2.48	0.006	1.93	0.006	0.30	3.88
12	Soil pH 5.5 + sand	1:1.5	5.55	840	4.83	6.88	2.18	0.006	1.39	0.005	0.30	3.45
13	Soil pH 5.5 + sand + gypsum	1:1.5	5.00	840	5.17	6.50	2.11	0.011	1.40	0.008	0.32	3.80
14	Soil pH 5.5 + sand	1:4	5.70	420	3.99	6.05	1.96	0.007	1.15	0.006	0.29	3.58
15	Soil pH 5.5 + sand + Mn	1:4	5.50	420	3.98	5.66	1.90	0.014	1.10	0.008	0.31	3.52
16	Soil pH 5.5 + sand + gypsum	1:4	5.05	420	4.01	6.08	2.14	0.015	1.59	0.008	0.31	3.00
17	Soil pH 5.5 + sand + Mn + gypsum	1:4	5.15	420	2.90	4.50	2.36	0.100	1.55	0.037	0.28	3.25
18	Soil pH 5.5 + sand	1:9	5.95	210	3.85	5.67	1.69	0.010	1.02	0.005	0.35	3.29
19	Soil pH 5.5 + sand + gypsum	1:9	5.00	210	4.67	6.23	2.38	0.011	1.62	0.007	0.35	3.61
20	Soil pH 6.5	1:0	6.20	3800	6.94	8.46	2.65	0.004	2.26	0.004	0.33	3.67
21	Soil pH 6.5 + sand	1:3.2	6.45	905	4.89	6.34	2.27	0.004	1.68	0.004	0.36	4.09
22	Soil pH 6.5 + sand + gypsum	1:3.2	5.65	905	4.92	6.69	2.35	0.005	1.87	0.005	0.33	4.18
23	Soil pH 6.5 + sand	1:15.8	6.40	225	4.13	6.14	1.80	0.005	1.12	0.004	0.36	3.41
24	Soil pH 6.5 + sand + gypsum	1:15.8	5.25	225	4.49	6.52	2.63	0.012	1.44	0.008	0.34	3.95
27	Peat pH 4.8 + sand		5.50	500	7.04	9.34	1.09	0.008	1.05	0.008	0.51	4.35
28	Peat pH 4.8 + sand + Mn		5.60	500	5.65	7.75	1.35	0.102	1.10	0.074	0.50	4.27
29	Peat pH 4.8 + sand		5.10	4000	5.89	8.99	1.78	0.008	1.45	0.007	0.50	4.04
30	Peat pH 6.5 + sand		6.25	500	5.57	7.80	1.51	0.006	1.08	0.007	0.38	4.10

* Gypsum applied at the rate of 2 tons per 2,000,000 pounds soil; Mn applied at the rate of 100 pounds Mn as $MnCO_3$ per 2,000,000 pounds soil.

† Exchangeable Ca content of the soil exclusive of any Ca applied in the form of gypsum.

‡ L.S.D. at 5 per cent point: first cutting, treatments 1–8 inclusive = 0.55 gm.; treatments 11–30 inclusive = 0.39 gm.; second cutting, treatments 1–30 inclusive = 0.90 gm.

of 28 per cent of the weight of the soil plus 15 per cent of the weight of the sand. This optimum moisture content was maintained throughout the experiment by frequent additions of distilled water. Treatments 27 to 30 inclusive were set up March 27, 1947, and distilled water was added in amount equal to 100 per cent of the weight of the peat plus 15 per cent of the weight of the sand. The treatments, replicated three times, were arranged in randomized blocks and seeded to Ranger alfalfa on March 29. The alfalfa was thinned after 2 to 3 weeks to 8 plants per pot. Frequent fumigation with azobenzene was required to control red spider.

The entire experiment was harvested when plants on the better treatments were in the early-bloom stage of growth. Plants on the poorer treatments were in the bud stage at the time. Four cuttings were made, June 3, July 2, August 2, and September 2. The plant material was dried at 70° C. for the determination of yields, and the leaves and petioles were removed and replicates composited for chemical analyses. The plant material was dry-ashed and analyzed for Ca and Mn by methods described by Peech (41), for P by the molybdivanadophosphoric acid procedure (27), and for Al and Fe by a modification of the procedures described by Peech and English (40). At the end of the experiment the soil was air-dried for the determination of pH and readily soluble Al, Mn, and Fe by methods of Peech and English (40). The results of the third and fourth cuttings are not reported because, after the second cutting, plants from treatments 3 to 8 inclusive were chlorotic and stunted. The application of N, Mo, Zn, and Cu to the soil or Cu, Zn, Fe, Mn, and Ca to the foliage failed to mprove the growth on these treatments.

Results

The dry weights of alfalfa and the chemical composition of the plants are recorded in table 1. Since the Al and Fe content of the plants varied little between treatments, the results of Fe and Al determinations are omitted. The P and N contents are given for only the second cutting because the results were essentially the same for both cuttings. As the Ca and Mn content of the plants varied greatly for the different treatments and cuttings, the analytical results for both cuttings are reported.

When the amount of exchangeable Ca in the unlimed soil (treatment 1) was reduced by diluting the soil with quartz sand (treatments 3 and 5), the growth of alfalfa increased as the amount of exchangeable Ca decreased. The degree of Ca saturation remained constant and the inert quartz sand could not have contributed to the nutrition of the plants; nor could the increased yield have been caused by improved aeration because of better physical condition of the soil, since the same trend was not observed when the limed soil was diluted with sand. The growth response obtained upon mixing the soil with sand cannot be attributed to the apparent increase in pH as measured at the end of the experiment by a standard procedure using suspensions prepared by taking one part of soil or soil + sand mixture to one part of water. Thus in the soil + sand mixtures the actual amount of soil per unit volume of water was smaller and consequently the higher pH value as reported in table 1 is simply due to the well-known dilution effect (42).

Obviously the low Ca supply in the soil was not the cause of the poor growth of alfalfa on the unlimed soil. On the contrary, the results would indicate that diluting the soil with sand alleviated some condition causing the poor growth of alfalfa in the unlimed Mardin soil. Examination of the rapid microchemical soil tests revealed that the readily soluble Al, Mn, and Fe decreased when the soil was either diluted with sand or was limed. The relationship between yield and readily soluble Al depicted in figure 1 show the same trends from dilution and liming; similar results were observed with Mn and Fe. The Mn content of the plants likewise decreased when the unlimed soil was diluted or limed, but the Al and Fe content remained about the same for all treatments. The results of soil and plant analysis would suggest that the increase in the yield of alfalfa when the control soil was diluted with sand may have been caused by a reduction in the amount of readily soluble Al, Mn, or Fe in the soil. The slight decrease in yield of alfalfa when the limed soil was diluted with sand was probably caused by a reduction in the supply of some nutrient element in the soil.

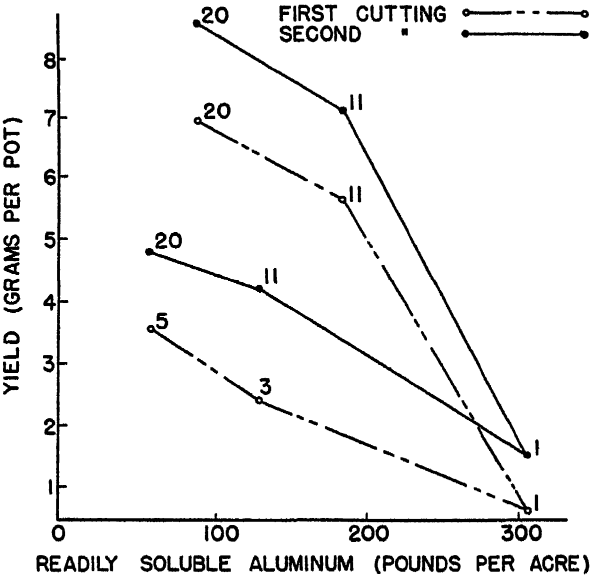

FIG. 1. RELATIONSHIP BETWEEN YIELD OF ALFALFA AND AMOUNT OF READILY SOLUBLE Al IN SOIL, EXPERIMENT I

Numbers on curves refer to treatments

Although alfalfa grew equally well on treatments 20 and 27, treatment 27 at pH 4.8 contained only 500 pounds exchangeable Ca whereas treatment 20 at pH of 6.5 contained nearly eight times as much. Conversely, treatments 1 and 27 each contained about the same amount of exchangeable Ca, but treatment 27 out-yielded treatment 1 many times. The results again suggest strongly that the poor growth of alfalfa on the unlimed Mardin soil was not due to the low supply of exchangeable Ca in the soil or to H-ion toxicity.

Treatments 27 and 29 were set up to compare the growth of alfalfa under different levels of exchangeable Ca in strongly acid soil (pH 4.8) free of readily soluble Al, Mn, and Fe. It was not possible to make this comparison for the first cutting because Mg-deficiency symptoms, due to the unfavorable Ca-Mg balance, appeared on plants in treatment 29. Additional Mg was added just before the first cutting. No Mg-deficiency symptoms were observed on the second growth of alfalfa. The yield of alfalfa in treatment 27 with only 500 pounds Ca per acre was equal to that in treatment 29 with 4,000 pounds exchangeable Ca.

The results of the treatments in which gypsum was used show clearly that the application of gypsum had no beneficial effect on the growth of alfalfa regardless of the amount of exchangeable Ca, soil reaction, or degree of Ca saturation. In only one out of 16 comparisons did the use of gypsum give an increase in yield significant at the 5 per cent level. Moreover, gypsum actually caused a decrease in yield in two comparisons.

Although the application of gypsum to the acid soil was found to increase the H-ion concentration and the amount of soluble Al (see experiment II), which might thus have overshadowed any benefit from Ca, it is pertinent to note that at pH 6.5 with only 225 pounds exchangeable Ca per acre, the application of gypsum failed to increase the yield of alfalfa. Thus satisfactory yield of alfalfa could be obtained even when the exchangeable Ca content of the soil was reduced to 225 pounds per 2,000,000 pounds.

It will be noted that the Ca content of the first cutting of alfalfa and total Ca uptake increased when the exchangeable Ca in the unlimed Mardin soil was reduced by diluting the soil with sand. The same effect was observed for total Ca uptake in the second cutting but not for the Ca content of the plants. Thus some factor other than the amount of exchangeable Ca or degree of Ca saturation was regulating Ca uptake by the plants on the unlimed soil. There was no consistent relationship between yield and the Ca content of the plants. Liming or diluting the Mardin soil increased both yield and Ca content of alfalfa in the first cutting, whereas, in the second cutting, either liming or diluting with sand increased yields but only liming the soil increased the Ca content of the plants. Alfalfa in the second cutting of treatment 5 contained only 0.72 per cent Ca; yet the plants appeared normal and exhibited no apparent Ca-deficiency symptoms. Indeed when gypsum was added to this treatment, the Ca content of the plants increased to 1.58 per cent but with no yield response. Alfalfa grown in the peat-sand culture with 500 pounds Ca at pH 4.8 (treatment 27) contained slightly more than 1 per cent Ca as compared to 2.26 and 2.65 per cent in plants grown in the Mardin soil limed to pH 6.5, but the yields were about the same for both treatments. In two cuttings the application of gypsum increased the Ca content of alfalfa in 10 out of 16 comparisons; only in one comparison when gypsum increased the Ca content of the plants was there an increase in yield (treatment 19, first cutting) and in another comparison (treatment 4, second cutting) gypsum decreased the yield. The results obtained from diluting the unlimed soil with sand, from the peat-culture treatments, and from applications of gypsum show conclusively that the Ca content of the plant in itself could not be used as a reliable index of the Ca status of the soil and that the poor growth of alfalfa in this unlimed soil was not due to Ca deficiency either in the soil or in the plants.

One hundred pounds of Mn, as $MnCO_3$, added to the unlimed soil that had been diluted with sand greatly reduced the growth of alfalfa, and growth was further reduced when gypsum was applied with $MnCO_3$ (cf. treatments 6 and 8). When the same amount of $MnCO_3$ was applied to the limed soil there was no reduction in growth unless gypsum was also added (treatment 17). The results point strongly to one of the reasons why applications of gypsum are not beneficial and may even prove injurious on acid soils high in exchangeable Mn and are in full agreement with the results reported by Fried and Peech (17).

Well-defined leaf symptoms were produced on plants grown in the peat-sand culture to which $MnCO_3$ had been added (treatment 28). The symptoms, which will be referred to as Mn toxicity, appeared as white areas on the margins of the leaves. Only slight Mn toxicity caused the veins to become white near the margins of the leaves (fig. 2, left leaflet); as the injury increased, small white spots developed near the leaf margins (fig. 2, terminal and right leaflets) until with severe injury 50 per cent or more of the leaf surface was affected (fig. 3). The center portion of leaflets similar to those in figure 3 continued to grow while the white marginal area discontinued growth; this caused a downward cupping of the leaf. As the leaves became older, necrotic spots often developed in the white marginal areas of the leaves.

These symptoms were used to identify Mn toxicity in alfalfa grown in the Mardin soil. They were present on all plants grown in the unlimed treatments, but injury was greatest on plants grown in the soil receiving applications of Mn (treatments 6 and 8). Typical symptoms of Mn toxicity observed on plants from treatment 6 are shown in figure 3. The Mn-toxicity symptoms in figure 2 are typical of those observed on 25 to 50 per cent of the leaves on plants from the control (treatment 1). In general, when the unlimed soil (treatment 1) was diluted with sand the extent of injury decreased, and when gypsum was applied to the unlimed soils the extent of injury increased. Symptoms of Mn toxicity were absent on plants grown in the limed soils except for treatment 17, which received applications of both $MnCO_3$ and gypsum.

The Mn-toxicity symptoms could not be correlated with the Mn or Ca content of the plant or with the Fe/Mn ratio. On the other hand, a scatter diagram of the relationship between the Ca/Mn ratio in the plant and the yield of alfalfa revealed a relatively good relationship between yield and the Ca/Mn ratio when the Ca/Mn ratio was less than 75 (fig. 4). Correlation coefficients calculated for the relationship between yield and Ca/Mn ratios of less than 75 were 0.82 and 0.89 for the first and second cuttings respectively. A closer analysis of several treatments, however, disclosed that the Ca/Mn ratio alone could not explain the poor yields on the unlimed soil; for example, the yields under treatments

1 and 8 were about the same for the first cutting, but the Ca/Mn ratio was much lower in plants in treatment 8; also the plants from treatment 28 had a much lower Ca/Mn ratio than those from treatment 1, yet growth was greater on treatment 28.

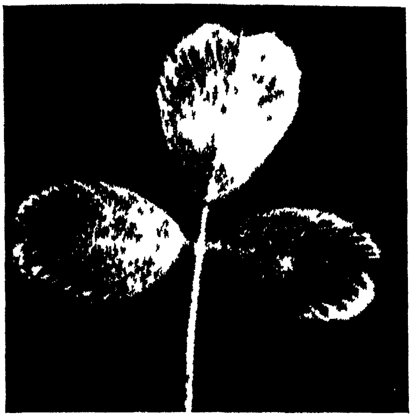

Fig. 2

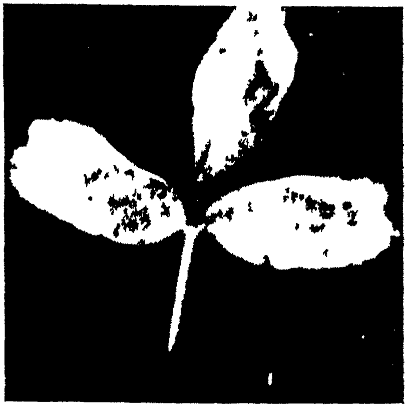

Fig. 3

Fig. 2 Symptoms of Mn Toxicity on Alfalfa Grown in Unlimed Mardin Soil, Treatment 1

Fig. 3. Symptoms of Mn Toxicity on Alfalfa Plants When 100 Pounds Mn Was Added to the Soil, Treatment 6

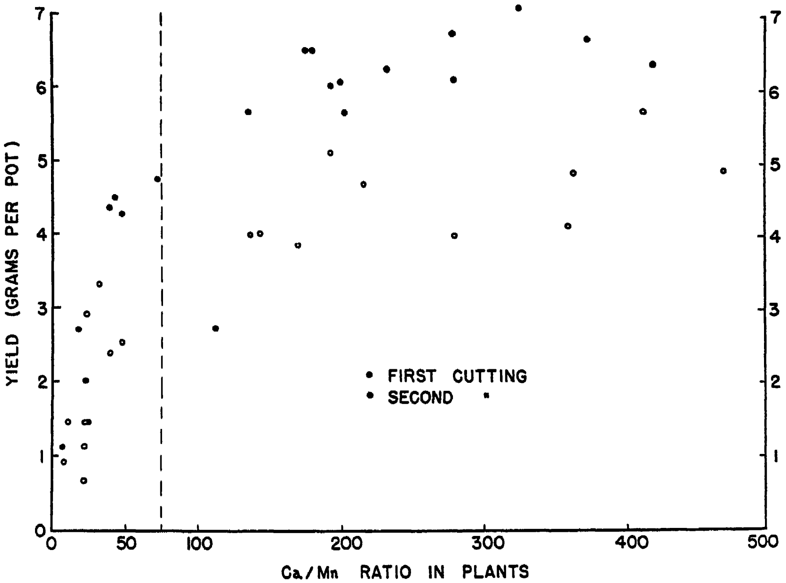

Fig. 4. Relationship Between Yield and Ca/Mn Ratio in Alfalfa Grown on Mardin Soil, Experiment I

Hewett (22) and Wallace (51) reported that Mn injury on plants grown in nutrient soltuion could be reduced by increasing the Ca concentration in solution. The gypsum treatments make possible determination of the influence of the Ca concentration in the soil solution on Mn absorption by alfalfa. In 20 comparisons the applications of gypsum decreased the Mn concentration in the plant only once; in fact, the Mn content was generally increased by gypsum treatments. Results of soil solution analysis presented later show that the application of gypsum not only increased Ca but also greatly increased Mn in the soil solution. Any direct antagonistic effect of the high Ca-ion concentration on Mn uptake was probably overshadowed by the increased Mn-ion concentration in the soil solution, because of liberation of exchangeable Mn by Ca ions.

Determination of the soil reaction revealed that the addition of gypsum increased the soil acidity by 0.25 to 0 75 pH units. The increase in acidity had but a slight effect on the amount of readily soluble Al, Mn, and Fe as shown by rapid microchemical soil tests. Dilution of the soil with sand decreased the amount of exchangeable Ca and readily soluble Al, Mn, and Fe, whereas liming the Mardin soil decreased the amount of readily soluble Al, Mn, and Fe but increased the exchangeable Ca. The results of the rapid microchemical soil tests support the view that the growth of alfalfa on the unlimed soil was not limited by the Ca supply.

EXPERIMENT II

From the results of experiment I it was apparent that the Ca supply was not so low as to limit the growth of alfalfa on the unlimed Mardin soil, and that there was sufficient amount of readily soluble Mn in the soil to produce symptoms of Mn toxicity on the plants. Manganese toxicity, however, did not seem to be the sole factor responsible for the poor growth of alfalfa obtained on the unlimed soil. Somers and Shive (47) and Hopkins, Pagan, and Ramırez-Silva (23) found that the Fe/Mn ratio on the plant and in the substrate rather than the absolute amounts of Fe and Mn determine the toxicity or deficiency of either of the two elements. McLean and Gilbert (30) reported that the hydrous oxides of Al may be toxic to plants, but Trenel (49) found that only Al ions injure the plants.

The objectives of experiment II were: first, to verify the beneficial effect of diluting the soil with sand observed in experiment I; second, to compare the effects of Al and Fe hydrous oxides with the sulfates of Al and Fe; and third, to obtain further evidence as to the influence of Mn toxicity on plant growth in the Mardin soil.

Materials and methods

Mardin silt loam from the A_p horizon was again used. Alfalfa was grown in the greenhouse in 1-gallon glazed pots filled with 4,000 gm. air-dried soil or an equivalent volume of soil plus sand, and all treatments received a basal fertilizer containing N, P, K, B, Mg, and S applied at the rate used in experiment I. Aluminum and Fe were added as hydrous oxides or as sulfates. The hydrous oxides were prepared by precipitation with NaOH from $Al_2(SO_4)_3$ and $FeCl_3$ solutions. The suspensions were washed with water until the Al suspension had a conductivity of 55×10^{-5} mhos and the Fe suspension had a conductivity of 10×10^{-5} mhos. The suspensions were standardized by evaporation to dryness and ignition to the oxide. The hydrous oxides were added as the suspension at the desired rates. Manganese was added as $MnCO_3$. The treatments are listed in table 2.

The experiment was set up on July 23 and seeded to Ranger alfalfa on August 6, 1947. Distilled water was added frequently to maintain a moisture content equal to 30 per cent of the weight of the soil plus 15 per cent of the weight of the sand. Cuttings were made on October 13 and November 14 when the plants were in the early-blossom stage. The plant material was dried at 70° C. and analyzed by procedures described in experiment I.

At the end of the experiment the soils were air-dried and the soil solution was removed from one replicate by the following procedure: The soil was passed through a 4-mesh screen and mixed thoroughly. The pot was again filled with the soil, and a "fine" fritted-glass filter stick was inserted with the end approximately in the center of the pot; distilled water was added to bring the moisture content to 50 per cent of the weight of the soil plus 25 per cent of the weight of the sand. After 24 hours, the soil solution was removed using a tension of 50 cm. of Hg. The soil solution was analyzed for NO_3-N, NH_3-N, Ca, Mn, Al, and Fe. Nitrogen, Al, and Fe were determined by rapid microchemical soil tests (40). Calcium was determined volumetrically as the oxalate, and Mn was determined by the periodate method (41).

Results

The yield data and the chemical composition of the plants are presented in table 2. Diluting the unlimed soil with sand gave a large yield response, as in experiment I, but the maximum yield was reached with the first dilution. Again as in experiment I, the application of gypsum did not increase the yield of alfalfa.

The application of hydrous oxides of Fe and Al produced a small decrease in yield in the first cutting but it was not significant at the 5 per cent level. These materials had little effect on the yield of the second cutting of alfalfa. On the other hand, the application of 150 pounds Fe as $FeSO_4$ decreased the yields in both cuttings, although the decrease was significant at the 5 per cent level only for the second cutting. When Al was added to the soil as the sulfate, the plants were slow to germinate and the cotyledons turned yellow soon after emergence. The leaves became a gray-green and the veins and petioles a reddish-purple. The plants died in a few weeks, and there was insufficient plant material for chemical analysis. The results would indicate that the hydrous oxides of Al and Fe in the Mardin soil at pH 4.75 have but a small influence on the growth of alfalfa, in contrast to the sulfates of Al and Fe, which are toxic even when applied in small amounts, despite the fact that these salts should undergo immediate hydrolysis with the formation of the respective hydrous oxides.

Manganese-toxicity symptoms were again observed on all unlimed treatments. Plants grown in Mn-treated soils showed increased Mn-toxicity symptoms over the control, as did plants grown in the soil treated with $FeSO_4$. The application of gypsum likewise increased the symptoms of Mn toxicity. Yields were not reduced when $MnCO_3$ was added to the soil. It is apparent that the excess of Mn did not appreciably reduce yields until the plants showed severe symptoms of Mn toxicity. The application of $FeSO_4$ did not reduce Mn toxicity as might be expected (23, 47).

TABLE 2

Plan of experiment II, and yield and chemical composition of alfalfa as affected by different treatments

NUMBER	TREATMENT PER 2,000,000 POUNDS SOIL	VOLUME RATIO SOIL: SAND	pH AT END OF EXPERIMENT	EXCHANGEABLE Ca PER 2,000,000 LB. SOIL*	YIELD OF ALFALFA PER POT†		CHEMICAL COMPOSITION OF ALFALFA					
							First cutting		Second cutting			
					First cutting	Second cutting	Ca	Mn	Ca	Mn	P	N
				lb.	*gm.*	*gm.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	Soil pH 4.75, control	1:0	4.35	600	3.50	2.11	1.54	0.140	1.42	0.081	0.31	5.00
2	Soil pH 4.75 + 2 tons gypsum	1:0	4.20	600	3.95	1.48	2.29	0.167	1.60	0.157	0.26	4.92
3	Soil pH 4.75 + sand	1:1	4.80	300	5.50	3.43	1.32	0.073	1.19	0.052	0.35	5.09
4	Soil pH 4.75 + sand + 2 tons gypsum	1:1	4.30	300	4.78	2.59	1.76	0.152	1.31	0.142	0.31	5.12
5	Soil pH 4.75 + sand	1:3	4.90	150	4.97	3.55	1.38	0.042	1.01	0.043	0.37	5.24
6	Soil pH 4.75 + sand + 2 tons gypsum	1:3	4.45	150	4.85	3.53	2.16	0.094	1.29	0.086	0.38	4.73
7	Soil pH 4.75 + sand + 150 lb. Mn‡	1:3	5.00	150	4.52	3.18	1.40	0.075	1.08	0.058	0.40	4.97
9	Soil pH 4.75 + sand + 300 lb. Fe§	1:3	4.95	150	4.06	3.52	1.39	0.031	1.04	0.040	0.36	5.03
11	Soil pH 4.75 + sand + 600 lb. Al§	1:3	5.05	150	4.12	3.47	1.44	0.031	0.98	0.043	0.37	4.98
15	Soil pH 4.75 + sand + 150 lb. Fe¶	1:3	4.70	150	4.03	2.65	1.22	0.110	1.02	0.080	0.35	4.95
16	Soil pH 4.75 + sand + 300 lb. Al¶	1:3	4.00	150	failure	failure	—	—	—	—	—	—
17	Soil limed to pH 5.5	1:0	5.35	2100	8.47	4.62	2.45	0.012	2.14	0.023	0.36	4.37
18	Soil limed to pH 6.5	1:0	6.15	3800	9.01	5.33	2.56	0.009	2.64	0.015	0.38	4.70

* Exchangeable Ca content of the soil exclusive of any Ca applied in the form of gypsum.

† L.S.D. at 5 per cent point: first cutting = 1.23 gm.; second cutting = 0.71 gm.

‡ Mn added as $MnCO_3$.

§ Fe and Al in treatments 9 and 11 added as the hydrous oxides.

¶ Fe and Al in treatments 15 and 16 added as $FeSO_4$ and $Al_2(SO_4)_3$ respectively.

The results of the soil solution analysis and rapid microchemical soil tests are given in table 3. The application of the hydrous oxides of Al and Fe did not increase the amount of readily soluble Al and Fe in the soil as revealed by rapid microchemical soil tests. The application of $Al_2(SO_4)_3$ greatly increased the readily soluble Al, whereas the application of $FeSO_4$ increased the readily soluble Fe but slightly. This would indicate that the soluble Fe and Al extracted by the acetate solution at pH 4.8 in accordance with the rapid microchemical soil tests (40) is of considerable ecological significance and should prove useful in assessing the lime needs of soils (42). Indeed, some of the unpublished studies[2] in this laboratory have shown that soluble Fe and Al extracted by the acetate solution at pH 4.8 are highly correlated with soil acidity.

The soil solution data indicate that the amount of Mn and Al was greatly reduced when the soil was either diluted with sand or limed. The amount of Ca in the soil solution decreased when the soil was diluted with sand but changed little when the soil was limed. The results suggest that the yield response to dilution with sand may have been caused, at least in part, by a reduction in Al and Mn toxicity.

TABLE 3

Chemical composition of soil solution and results of rapid microchemical soil tests as affected by different treatments, Experiment II

TREATMENT NUMBER	COMPOSITION OF THE SOIL SOLUTION						RESULTS OF RAPID MICROCHEMICAL SOIL TESTS, PER 2,000,000 POUNDS SOIL		
	NO_3-N	NH_4-N	Ca	Mn	Al	Fe	Mn	Al	Fe
	ppm.	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*lb.*	*lb.*	*lb.*
1	112	11.0	81.7	7.35	1.91	0.27	85	350	60
2	162	11.0	502	45.4	9.97	0.29	105	315	50
3	0.0	5.0	11.7	1.25	0.25	0.18	50	125	25
4	11.0	8.0	556	40.5	6.82	0.21	55	140	22
5	0.0	3.5	9.1	1.36	0.23	0.19	28	75	10
6	0.0	6.5	593	24.9	4.05	0.36	28	65	10
7	0.0	2.8	6.8	0.43	0.11	0.22	65	65	14
9	0.0	12.5	3.8	0.14	0.18	0.52	26	70	10
11	12.5	2.5	24.6	0.39	0.02	0.14	29	70	11
15	12.5	1.3	28.7	7.15	0.81	0.14	30	80	17
16	75.0	115	182	53.2	65.0	0.29	40	160	16
17	0.0	2.8	44.0	0.14	0.18	0.23	45	200	22
18	0.0	9.0	73.2	0.00	0.02	0.16	20	90	9

The concentrations of Al, Mn, and Ca in soil solution were markedly increased when gypsum was added to the soil, as has been noted by Fried and Peech (17). The Al and Mn concentrations were also increased when $Al_2(SO_4)_3$ or $FeSO_4$ was applied. This would explain why gypsum aggravated Mn toxicity in both experiments I and II and why the application of hydrous oxides of Al and Fe had no influence on the growth of alfalfa, whereas the application of $Al_2(SO_4)_3$ caused a crop failure and $FeSO_4$ decreased alfalfa yields. The survival of alfalfa on gypsum-treated soils which showed high concentrations of Al and Mn in the soil solution may be due to Ca antagonism resulting from the concurrent increase in Ca concentration in the soil solution.

[2] Lunin, J. Some factors affecting the solubility of aluminum, iron, and manganese in soils and clays. 1949. [Unpublished Ph. D. thesis, Cornell University, Ithaca, New York.]

Comparison of treatments 1, 17, and 18 (table 3) shows that there should have been an adequate supply of Ca in the unlimed soil; nevertheless, the Ca content of the plants from the unlimed soil was considerably lower than that from the limed soils. This effect may again be related to ion antagonism; the high concentrations of Al, Mn, or H may have reduced the Ca uptake by the plants.

High concentrations of NH_3-N in the soil solution resulted when nitrification was apparently inhibited at very low pH values (treatment 16). Low concentrations of both NH_3-N and NO_3-N were associated with high-yielding treatments and/or treatments low in organic matter (soils diluted with sand).

DISCUSSION

The results of this investigation show that the poor growth of alfalfa on the unlimed Mardin soil cannot be attributed to the low exchangeable Ca content of the soil or to the low degree of Ca saturation. The growth of alfalfa increased when the exchangeable Ca content was reduced by diluting the soil with sand, and there was no yield response to the application of gypsum at any level of exchangeable Ca. Moreover, the growth of alfalfa was normal on a peat-sand culture containing less exchangeable Ca than the unlimed soil.

Since the application of lime to acid soils may increase the Ca content of the crop (2, 16, 37), it has often been assumed that the beneficial effect of liming is due to the increased supply of Ca as a nutrient. In the present investigation, however, the Ca content of alfalfa was not correlated with yield. For example, though the yield of alfalfa increased when the soil was either limed or diluted with sand, the Ca content of the plant increased when the soil was limed and in three instances out of four decreased when the soil was diluted with sand. The application of gypsum generally increased the Ca content of plants without increasing yields. In experiment I the Ca content of plants grown in the Mardin soil limed to pH 6.5 was more than twice that of plants grown in the peat-sand culture at pH 4.8 containing only 500 pounds exchangeable Ca per acre, yet the yields were the same for both treatments. It was also noted that the Ca content of alfalfa could vary from less than 1 per cent to nearly 3 per cent without apparent symptoms of Ca deficiency.

Calcium-manganese as well as Ca-Al antagonism in plants has been suggested by Hewitt (22) and others (18, 26) based on work with nutrient solutions. When an attempt was made to evaluate Ca-Mn antagonism in the Mardin soil by adding $MnCO_3$ with and without gypsum, it was found that gypsum actually aggravated Mn toxicity. Although no soil solution studies were made in experiment I, the failure of gypsum to antagonize Mn toxicity may be explained in light of the soil solution data obtained in experiment II. Gypsum greatly increased the Mn concentration in the soil solution in experiment II as a result of the replacement of exchangeable Mn by Ca ions in solution. Thus it was not possible to make a direct evaluation of Ca-Mn antagonism from the experiment. There was, nevertheless, indirect evidence in experiment II of Ca-Mn and Ca-Al antagonism. The addition of gypsum to the unlimed soil increased Mn in the soil solution from 7.35 to 45.4 ppm. and increased Al from 1.91 to 9.97 ppm. without influencing the yield of alfalfa. The survival of the plants in this instance may well be the result of Ca-Mn and Ca-Al antagonism in the presence of the high Ca concentration (more than 500 ppm.) in the soil solution.

The soil in experiments I and II was fertilized with N and P to eliminate these nutrients as limiting factors to plant growth under acid soil conditions, and this was substantiated by the plant analyses. Molybdenum was not applied initially, but no response was obtained when Mo was added subsequently to several treatments. The H-ion concentration, *per se*, was not a major factor controlling the growth of alfalfa in the experiment, inasmuch as alfalfa grew very well in the peat-sand culture at pH 4.8 with only 500 pounds exchangeable Ca per acre. Thus the primary reason for the poor growth of alfalfa on the unlimed soil cannot be attributed to a deficiency of Ca, N, or P, or to toxicity of the H ion. Although definite Mn-toxicity symptoms were observed on plants grown in the control treatment, a critical examination of the data revealed that the extent of Mn toxicity of such plants was not sufficient to account for the greatly reduced growth. There is, therefore, good indication that the excessive concentration of Al in soil solution in the unlimed soil (control) was a major factor limiting the growth of alfalfa on the soil.

SUMMARY

Two greenhouse experiments were conducted to determine the influence of the exchangeable Ca supply, soil acidity, Mn, Al, and Fe as factors affecting the growth of alfalfa on Mardin silt loam having a pH of 4.75 and containing 600 pounds exchangeable Ca per 2,000,000 pounds of soil.

When the exchangeable Ca content was reduced to 150 pounds per 2,000,000 pounds of soil by diluting the soil with sand, the yield of alfalfa increased as much as 500 per cent. The growth of alfalfa on a peat-sand culture at pH 4.8 containing 500 pounds exchangeable Ca was as good as that on the Mardin soil limed to pH 6.5 and containing 3,800 pounds exchangeable Ca per acre. The poor growth of alfalfa on the unlimed soil was, therefore, not due to the low exchangeable Ca supply in the soil or to the low Ca content of the plants.

The application of gypsum to the soil at varying levels of exchangeable Ca and at different pH values not only failed to increase the yield of alfalfa but caused a reduction in yield when the soil was high in exchangeable Mn. The Mn and Al concentrations in the soil solution were greatly increased by the application of gypsum to the soil.

Symptoms of Mn toxicity appeared on the plants when the Ca-Mn ratio in the plants was less than 75. Manganese toxicity was observed on all plants growing on the unlimed soil. The toxicity was reduced when the soil was diluted with sand and was increased when gypsum was applied to the soil.

Aluminum and Fe added to the soil as the hydrous oxides had little influence on plant growth, but when Al and Fe were added as the sulfates, the yield of alfalfa was reduced. The amount of readily soluble Al and Mn, as determined by rapid microchemical soil tests, and the concentration of these two elements in soil solution were decreased by either liming the soil or diluting the soil with quartz sand. The beneficial effect of liming or diluting the soil with sand may be attributed to the decrease in concentration of Al and Mn in soil solution.

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BOOKS

Annual Review of Biochemistry, Volume 19. Edited by J. Murray Luck. Annual Reviews, Inc., Stanford, California, 1950. Pp. 596. Price $6.

By reason of the publication of "Annual Review of Plant Physiology," topics such as mineral nutrition, growth substances, and respiration of plants, which previously were included in biochemistry, are largely eliminated. The current volume contains 22 papers on oxidations, enzymes, chemistry of carbohydrates, lipids, hormones, amino acids, and nucleic acids, metabolism of carbohydrates, fats, and proteins, vitamins, human nutrition, muscle, neoplastic tissue, blood, pigments, immuno-chemistry, antibiotics, and chromatography. The work of some 6,000 authors is reviewed. Soil-plant scientists will be especially interested in the discussion of antibacterial substances from higher plants. These include allicin from onions, lupulon from hops, rhein from rhubarb, tomatine from tomatoes, and a number of others. Presumably to reduce the size of the volume and keep down costs, a smaller type than formerly was used. The general excellence of past reviews has been maintained in this volume.

The Autobiography of Robert A. Millikan. By Robert A. Millikan. Prentice-Hall, Inc., New York, 1950. Pp. 311, plates 9. Price $4.50.

It was only by chance that Millikan became a physicist instead of a professor of Greek. But once the science was opened up to him, he found himself fascinated by its possibilities and soon moved into a position of leadership in this field of research. The many thousands who have studied Millikan and Gale's readily understandable text will know that this autobiography is interesting reading. No matter what one's field of research, he will find highly stimulating the story of the rise of this small-town boy to the top in physics. The last chapter sums up Millikan's philosophy on the need for the spirit of religion and the spirit of science to work hand in hand toward the solution of the ills of mankind.

The Biochemistry of B Vitamins. By Roger J. Williams, Robert E. Eakin, Ernest Beerstecher, Jr., and William Shive. Reinhold Publishing Corporation, New York, 1950. Pp. 741. Price $10.

This is American Chemical Society Monograph No. 110, and is dedicated to The Clayton Foundation for Research for its generous support of studies on this vitamin. The authors have endeavored to produce a volume that would be readily intelligible to scientists in related fields of research. The material consists of a careful survey of recent work on vitamin B, with suggestions for fruitful fields for investigation. The subject is considered in four sections, entitled "Characterization, distribution, assay, and biogenesis of B vitamins"; "Catalytical functions"; "Role in plants and animals"; and "Comparative biological activities." A statement of special interest to soil-plant-animal scientists reads: "The anemias in cattle resulting from cobalt deficiency can be corrected only by oral administration." Appended to each of the 25 chapters is a long list of references, which total more than 3,500 for the entire volume. The material is so well presented and the coverage is so complete, as of the moment, that everyone connected with this and related fields of research will want to have a copy handy.

Colloid Chemistry, Volume 7. Edited by JEROME ALEXANDER. Reinhold Publishing Corporation, New York, 1950. Pp. 734. Price $15.

Volume 7 consists of 43 papers written by 45 contributors from widely distributed parts of the earth. It deals with theory and methods, biology and medicine, and technological applications of colloid chemistry. References are given to the work of some 1,500 research specialists. Two chapters are of special interest to soil scientists: Organophilic Clays, by Ernst A. Hauser, and Theory of Colloidal Behavior in Soils, by Amar Nath Puri. Every scientist will find one or more chapters that will be of immediate interest. Alexander's contributions on successive levels of material structure and catalysts and neocatalysts in biology and medicine, of a more philosophic nature, include, among other matters, reference to the well-known discussion between Mephistopheles and the student about the usefulness of words in avoiding a direct issue. The material in this volume is of the usual high standard of excellence of the series.

Colloid Science. By JAMES W. MCBAIN. Reinhold Publishing Corporation, New York, 1950. Pp. 450. Price, trade, $8; text, $6.

Arthur B. Lamb, commenting in the foreword of this book, points out that a knowledge of colloid science is essential to a clarification of the physics and chemistry of a large part of the universe to which man is continuously exposed. The author of the book has endeavored to present the subject in the light of that relationship. Its 24 chapters deal with general principles, which are then applied to soaps, proteins, lubricants, textiles, sugars, rubbers, resins, clays, and aerosols. The chapter on clays deals with classification, mineral species, x-ray examination, thermal analyses, electron microscope, cation exchange, swelling, flocculation, rheology, uses of clays, and comparisons with other colloids. For the entire volume, the work of some 1,200 authors is reviewed. The book is lucidly written, well illustrated, and gives an excellent presentation of the knowledge in this field.

Forage and Pasture Crops. By W. A. WHEELER. D. Van Nostrand Company, Inc., New York, 1950. Pp. 752. Price $8.

This handbook on grasses and legumes for forage was prepared under the auspices of The Field Seed Institute of North America. The material presented is encyclopedic in nature. The first part covers the general principles of grass and legume adaptations, use of fertilizers, inoculation, green manuring, pasture management, hay and silage making, and the selection and breeding of forage and pasture crops. The second part goes into detail concerning the several legumes, discussing their origin, adaptations, methods of production, weeds, diseases, and insects affecting them, their use for hay, pasture, silage, and seed, and the varieties and strains. Part three, on the grasses, follows the same general pattern as part two. Part four consists largely of tabular material on seed and of a selected list of references, state by state, and for the U. S. Department of Agriculture. The work of more than 1,000 soil and plant scientists is included among these references. The book is a highly important contribution to the literature on this subject, and it should be made easily available to all soil-crop specialists.

Highlights of Soil Science. By A. N. PURI. Hoitsema Brothers, Groningen, The Netherlands, 1950. Pp. 80. Price, paper-bound, $0.60.

This is, in effect, a very brief presentation of the more important conclusions contained in the author's larger volume, "Soils, Their Physics and Chemistry" (reviewed in SOIL SCIENCE 69: 165). The author's expressed intention is to "present the highlights of soil science against a background of classical chemistry."

Reconnaissance Soil Survey of Japan, Kyota Area. By EUGENE P. WHITESIDE. General Headquarters Supreme Commander for the Allied Powers, Natural Resources Section, Report No. 110-C, Tokyo, 1950.

This report, the third of a series, deals with an area of 37,757 square kilometers in which the population density averages 343 persons per square kilometer. Only about 20 per cent of the land area is inhabited. The most important crop is rice. The predominant natural vegetation is mixed evergreen and deciduous trees. The soils are relatively young with weakly developed profiles. About 80 per cent of the area is hilly to mountainous. The 29 soil associations recognized are shown on appended soil maps. The alluvial soils are most important agriculturally. Planosols, ando soils, red-yellow podzolic soils, and lithosols are found at successively higher levels.

Rothamsted Experimental Station Report for 1949. Harpenden. Pp. 178. Price paper-bound, 5/—(foreign postage extra).

As usual, the report contains a great variety of material of interest and value to soil-plant specialists. Among the many matters discussed are deep plowing, radioactive tracers, spectrographic analyses of soils for molybdenum, a wind tunnel for study of dispersal of fungus spores, weather records showing total rainfall of 20.28 inches for 1948–49, tainting of root crops from use of benzene hexachloride, and use of salt as fertilizer on beets and barley. References to 194 publications for the year are appended.

Soil Fertility and Sewage. By J. P. J. VAN VUREN. Dover Publications, Inc., New York, 1948. Pp. 236, figs. 28. Price $4.50.

The author gives a very interesting account of experiences in composting town wastes in South Africa. After much trial and error, he succeeded in developing procedures by which dry refuse and night soil were made into satisfactory compost, with control of flies and odors. His data indicated that for a population of 10,000 there were 250 cubic feet dry refuse and 500 gallons night soil daily. To take care of these materials required 10,000 cubic feet of trench, which, with the necessary platforms, was constructed at a cost of about $1,200. The costs of the finished product were estimated at $1 a cubic yard for a product that sold for

$1.50. The book merits study in connection with the disposal of city wastes in this country. It should be possible to develop mechanical means by which this could be accomplished with greater nicety and economy than with hand labor.

Soils of the Netherlands. By C. H. EDELMAN. North-Holland Publishing Company, Amsterdam, 1950. Pp. 177, figs. 65.

This volume was written as a special favor to the foreign visitors to the Fourth International Congress of Soil Science, which held its formal meetings in Amsterdam July 24 to August 1, 1950. The purpose of the author was to provide a background of information on the soils of The Netherlands in preparation for the field trips that were taken August 2 to 12. The author presents a concise description of The Netherlands and the general classification of the soils. He then deals more specifically with the sands, river-clay soils, peats, marine clays, estuary soils, and Zuiderzee-bottom soils. The book is of special interest by reason of the high degree of intensity of the agriculture of The Netherlands and the large amount of land that has been reclaimed, partly from those areas from which peat had been harvested for fuel and partly from others that were formerly beneath the sea. A provisional soil map on the 1:400,000 scale is appended. The book admirably served the purpose for which it was intended.

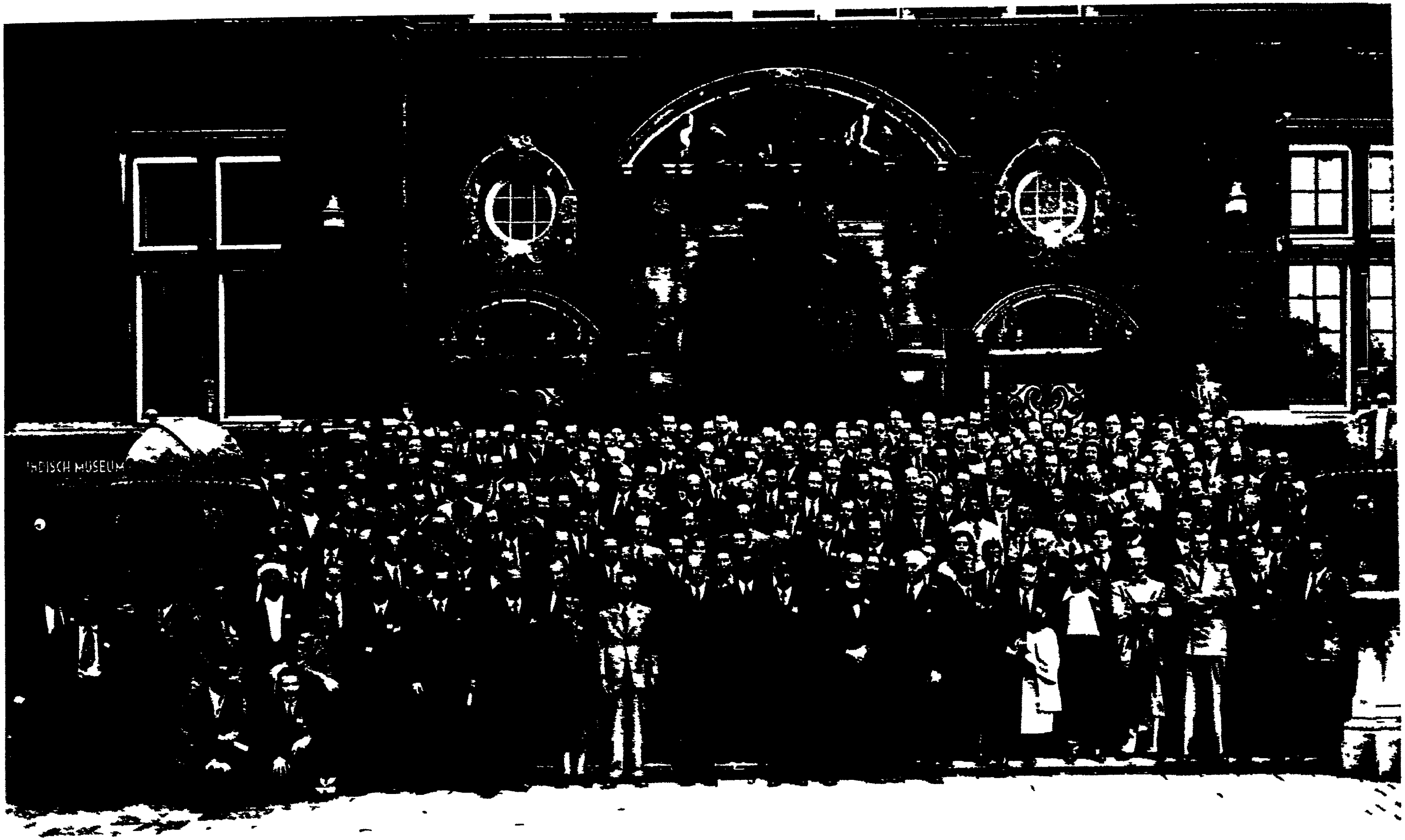
Titanium, Its Occurrence, Chemistry, and Technology. By JELKS BARKSDALE. The Ronald Press Company, New York, 1950. Pp. 591, figs. 15. Price $10.

It seems strange that so little attention has been paid to titanium as a constituent in soils and plants, since it is ninth in abundance of the elements in the lithosphere, constituting 0.62 per cent of the total. The soil's content lies between the limits of about 0.50 and 1.50 per cent. Titanium in plants has been reported to be as high as 0.017 per cent, and there is some evidence that the element is beneficial. Legumes are relatively high in titanium, notably in the nodules. Some 2,800 references are contained in this volume, which covers every phase of titanium chemistry and presents the first detailed discussion of this element. For having assembled such an excellent volume of important information, the author is entitled to the thanks of all those who are interested in titanium.

Fourth International Congress of Soil Science Transactions, Volume 2. Hoitsema Brothers, Groningen, The Netherlands, 1950. Pp. 266.

This volume contains two general lectures on soil structure and on soil moisture and evaporation by Richard Bradfield and R. H. Schofield, respectively. It also contains 79 additional papers that were presented before the sections on soil physics, clay minerals, soil chemistry, soil biology, soil fertility, tropical and subtropical soils, land classification and evaluation, and saline soils. Taken in conjunction with volume 1 (reviewed in SOIL SCIENCE 70: 165), these papers present a good summary of some of the more important aspects of current soil science.

THE EDITORS.



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Members of Fourth International Congress of Soil Science, Which Met at Amsterdam, Netherlands, July 24 to August 1

SOIL SCIENCE

VOLUME 70 December 1950 NUMBER 6

RADIATION INJURY TO PLANTS GROWN IN NUTRIENT SOLUTIONS CONTAINING P^{32}

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U. S. Department of Agriculture[1]

Received for publication May 24, 1950

During recent years, many investigators have utilized radioactive isotopes in experiments designed to study the mineral nutrition of plants. Although radiation from the disintegrating atoms of a radioisotope is capable of damaging living tissue, it has been commonly assumed that serious plant injury is not caused by the relatively small amounts of radioactive materials used in tracer techniques. This assumption was challenged by Russel and Martin (5), who showed a significant effect on the dry weights of roots of young barley plants when grown for only 6 days in nutrient solutions containing as little as 10 microcuries P^{32} per liter. This level of radioactive isotope is no higher than the concentrations employed in many plant experiments and is, in fact, appreciably lower than levels that have sometimes been advocated as satisfactory (1).

Because of the widespread use of radioisotopes in plant studies, and because many nutrition problems are not easily examined by other techniques, it is important to explore thoroughly the possibility that radiation damage to plants may occur under the customary experimental circumstances. If such damage does occur, then it becomes equally important to determine under what conditions the damage produced is serious enough to affect the validity of conclusions drawn from the data obtained.

GENERAL METHODS

The experiments reported in this paper were all carried out with young barley plants (variety Wong) grown in nutrient solutions in a constant-temperature chamber illuminated with fluorescent lights. Alternate white and daylight, 30-watt fluorescent light tubes were mounted in a panel suspended over a table upon which the plants were grown. The light intensity at the leaf surfaces was approximately 1,000 foot-candles. An automatic time switch provided for 16 hours of light and 8 hours of darkness. The temperature was maintained at 80°F., and the relative humidity was approximately 50 per cent.

The following procedure was used to grow the experimental plants. Barley seeds were soaked for 6 hours in tap water through which air was constantly bubbled. The seeds were then transferred to stainless steel screens supported in flat Pyrex baking dishes containing tap water, the surface of which was adjusted to the level of the screen. A porcelain tray was inverted over the assembly to ensure darkness and reduce evaporation. Soaking and germination were carried on in the laboratory where the temperature was approximately 80°F. When the barley sprouts were about 1 inch long (second morning after soaking) the porcelain tray was removed. After a few hours in the diffused light of the laboratory, the dishes of seedlings were moved to the light chamber. On the fifth day after the seeds had been soaked, the seedlings were transplanted to corks, each cork containing six plants.

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[1] Bureau of Plant Industry, Soils, and Agricultural Engineering, Beltsville, Maryland This investigation was supported in part by the U. S. Atomic Energy Commission.

Commercially available No. 10 cans, lined with enamel, were used as containers for the experimental nutrient solutions. In some instances the height of the can was cut down to approximately 4¾ inches, so that its capacity was reduced to about 1,800 ml. from the normal 3 liters. New cans were used for each experiment. A 7-inch Masonite square, drilled with four 2⅜-inch holes served to support four corks of plants. An additional, smaller hole in the Masonite square was provided for introduction of an air line. Each board of four corks (24 plants) was considered an experimental unit. Each treatment was replicated three times. All nutrient solutions were prepared from water that had passed through a demineralizer.

The basic nutrient solution used was one that Dean and Rubins (2) had found suitable for the light conditions prevailing in this light chamber. It contained per liter: magnesium sulfate, 0.5×10^{-3} moles; calcium nitrate, 0.5×10^{-3} moles; calcium sulfate, 1.0×10^{-3} moles; potassium sulfate, 0.7×10^{-3} moles.

Phosphorus was supplied as KH_2PO_4, the amounts differing for the various treatments. Iron was furnished the plants by spraying the leaves with 10 ppm. ferric tartrate solution every second or third day. Since the plants were grown for comparatively short periods, no other minor elements were found necessary.

The partly exhausted nutrient solutions were discarded at frequent intervals and replaced by fresh solutions. At each change, allowance was made for decay of the P^{32}, and a sufficient quantity of the isotope stock solution was added to bring the P^{32} content of the new solutions up to the original levels. All of the radioactive phosphorus used was the separated isotope prepared by pile irradiation of sulfur and listed in the catalog of the Isotopes Division of the Atomic Energy Commission as Item S-3. The routine analytical reports accompanying the isotope shipments from the Oak Ridge National Laboratories were used as the basis for dilution to the desired P^{32} concentrations. No attempt was made to determine absolute P^{32} concentrations, but comparative counts on the various shipments showed good agreement. All counting of plant samples and nutrient solutions was carried out with a proportional counter.

EXPERIMENTAL RESULTS

Preliminary experiments had shown that barley plants could be seriously damaged by P^{32} in the nutrient solutions, and had indicated that the P^{32}/P^{31} ratio (specific activity) was as important as the total amount of P^{32} in the solution bathing the roots of the plant. To determine the approximate concentration ranges of P^{32} and P^{31} at which appreciable damage might occur to young barley plants, the following experiment was carried out.

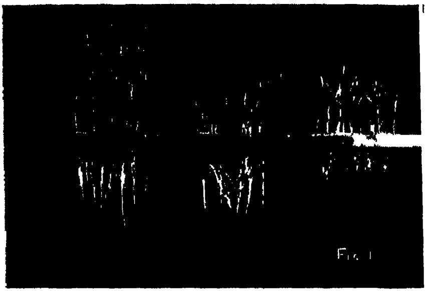
Growth and phosphorus content

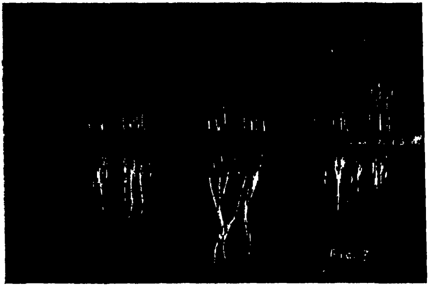
Five-day-old barley plants were grown as described earlier, transplanted to corks, and placed in the various test solutions. At the time of transplanting, the first leaf of the plant was nearly fully expanded and the second leaf was just starting to emerge from the sheath. The nutrient solutions used were divided into four series on the basis of their $H_2PO_4^-$ content, being respectively 5×10^{-6}, 5×10^{-5}, 5×10^{-4}, and 5×10^{-3} molar with respect to phosphate. There were three treatments in each of these series. They contained respectively 0, 50, and 200 microcuries P^{32} (as $H_2PO_4^-$) per liter. All solutions were discarded and replaced by fresh solutions every fourth day. Forced aeration of the cultures was not employed. The plants were grown for 12 days before being harvested, at which time they each had three well-developed foliage leaves, the last two of which had made nearly all of their growth since the beginning of the experimental treatment. In some of the plants, a fourth leaf was just starting to emerge. At harvest, the lengths of the second and third leaves were recorded and the dry weights of tops and roots were taken separately. Figures 1, 2, 3, and 4 show representative plants at harvest time. Table 1 presents the yield data.

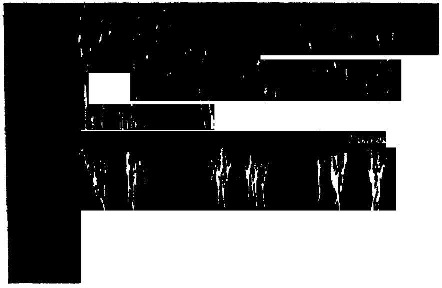
Obviously, the length of the newer leaves is a more sensitive criterion of damage than dry weight of either tops or roots. This is not unexpected, since a considerable part of the dry weights of the tops and the roots of the plants at harvest is due to the weights of those same parts at the time the experiment started, whereas the leaf measurements deal only with growth subsequent to treatment. Since there was no evidence of atrophy of the original plants, the measurements dealing with new growth show differences between treatments more effectively than measurements dealing with the entire plant.

An analysis of the data shows that the P^{32} level and the P^{31} level of the nutrient solutions have each had a significant effect upon the length of leaves, dry weight of tops, and dry weight of roots. On the basis of the leaf measurements, both the 50- and the 200-microcurie treatments on the 5×10^{-6} and 5×10^{-5} molar phosphate series caused significant damage to the plants. On the basis of dry weight of tops, significant damage appeared only in the 200-microcurie treatments on the 5×10^{-6} and 5×10^{-5} molar phosphate series. When judgment was made on the basis of dry weights of roots, only one treatment, that employing 200 microcuries of P^{32} in a 5×10^{-6} molar phosphate solution, produced significant injury. No damage was apparent by any criteria on the 5×10^{-4} or 5×10^{-3} molar phosphate series.

In a second experiment, the effect of somewhat lower levels of P^{32} upon barley plants was studied when the plants were grown in a nutrient solution which contained 2×10^{-5} moles $H_2PO_4^-$ per liter. The barley plants were again 5 days old when the experiment was started and were grown in the experimental solutions for 15 days. A stream of filtered air was continuously bubbled through each solution and all solutions were discarded and replaced every second day. Figure 5 shows representative plants on the harvest date, and figure 6 the average length of the second, third, and fourth leaves at harvest.







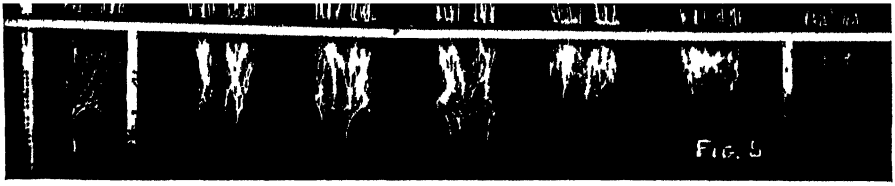


Fig. 1. Barley Grown in Nutrient Solution 5 × 10^{-6} Molar in Phosphate
Fig. 2. Barley Grown in Nutrient Solution 5 × 10^{-5} Molar in Phosphate
Fig. 3. Barley Grown in Nutrient Solution 5 × 10^{-4} Molar in Phosphate
Fig. 4. Barley Grown in Nutrient Solution 5 × 10^{-3} Molar in Phosphate
Figs. 1–4, left to right: 0, 50, and 200 microcuries P^{32} per liter
Fig. 5. Barley Grown in Nutrient Solution 2 × 10^{-5} Molar in Phosphate
Left to right: 0, 2, 4, 8, 16, 32, and 64 microcuries P^{32} per liter

The measurements show that the length of the second leaf was significantly affected only at the two highest levels of P^{32}; namely, 32 and 64 microcuries per liter, but that the length of the third leaf was affected at still lower levels. In the 64-microcurie treatment, the third leaf did not emerge at all. The third

TABLE 1

Effect of P^{32} in nutrient solutions on growth of barley plants

MICROCURIES P^{32} PER LITER OF NUTRIENT SOLUTION	GROWTH CRITERIA			
	Moles P^{31} per Liter of Nutrient Solution			
	5×10^{-6}	5×10^{-5}	5×10^{-4}	5×10^{-3}
	Av. total length (cm.) of 2nd and 3rd leaves (per plant)			
0	21.99	27.87	25.73	26.26
50	10.49**	24.46*	29.78	24.96
200	4.51**	9.32**	24.40	25.32
	Av. dry weight (gm.) of tops (per 24 plants)			
0	0.55	0.74	0.64	0.66
50	0.50	0.71	0.83	0.64
200	0.39**	0.51**	0.64	0.63
	Av. dry weight (gm.) of roots (per 24 plants)			
0	0.23	0.24	0.23	0.22
50	0.25	0.28	0.25	0.22
200	0.13**	0.20	0.25	0.21

* Significantly lower than respective control at 5 per cent level.

** Significantly lower than respective control at 1 per cent level.

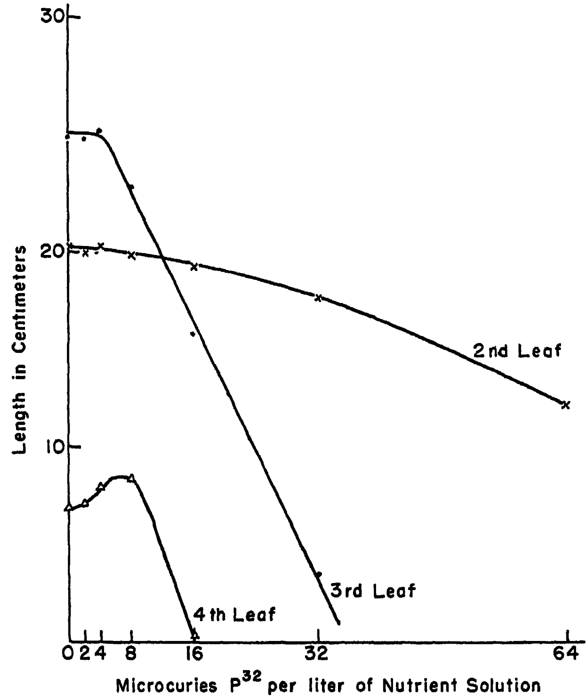


FIG. 6. EFFECT OF P^{32} CONCENTRATION OF NUTRIENT SOLUTION ON LENGTH OF BARLEY LEAVES

leaves of plants grown on solutions containing 8 or more microcuries P^{32} per liter were significantly shorter (1 per cent level) than the third leaves of the plants of the controls. The lengths of the fourth leaves of the 2-, 4-, and 8-millicurie treatments showed increases above the lengths of the corresponding leaves of the control plants, but the increases were not significant, and the fourth leaves were greatly shortened on the plants grown in the 16-microcurie treatment. There were no emergent fourth leaves on the plants grown on solutions containing 32 or 64 microcuries per liter.

TABLE 2

Effect of different levels of P^{32} in a 2×10^{-5} molar phosphate nutrient solution on growth of barley

MICROCURIES P^{32} PER LITER OF NUTRIENT SOLUTION	DRY WT. OF TOPS (24 PLANTS)	DRY WT OF ROOTS (24 PLANTS)
	gm.	*gm.*
0	1.79	0.63
2	1.71	0.60
4	1.79	0.62
8	1.74	0.58
16	1.50**	0.67
32	1.01**	0.68
64	0.94**	0.43*

** Significant at 1 per cent level.

TABLE 3

Phosphate absorption by barley from 2×10^{-5} molar phosphate solution

MICROCURIES P^{32} PER LITER OF NUTRIENT SOLUTION	PHOSPHORUS ABSORBED BY 24 PLANTS IN 48 HOURS*				
	2nd Period	3rd Period	4th Period	5th Period	6th Period
	mgm	*mgm.*	*mgm.*	*mgm.*	*mgm.*
2	1.03	1.05	1.04	1.06	1.05
4	1.03	1.04	1.07	1.07	1.07
8	1.01	1.05	1.07	1.08	1.08
16	1.04	1.05	1.08	1.08	1.08
32	1.02	1.00	1.07	1.07	1.07
64	0.99	1.01	1.07	1.07	1.06

* Total phosphorus available per 48-hour period was 1.10 mgm.

Table 2 shows the dry weights of tops and roots. Once again, both are less sensitive criteria of plant damage than the leaf measurements. The dry weight of tops was significantly less than the dry weight of the tops of the control plants for the three highest levels of treatment but only the 64 microcuries per liter solution produced plants with dry weight of roots significantly less than that of the control. Table 3 shows the total phosphate utilization by the plants during five of the seven 48-hour periods between solution changes. The data were obtained by P^{32} counts of the solutions before and after use. There were no significant differences in amounts of phosphorus absorbed.

In a third experiment, barley plants were grown in nutrient solutions 1 × 10^{-3} molar for phosphate. The solutions for the various treatments contained 0, 4, 8, 16, 32, 64, and 128 microcuries P^{32} per liter, respectively. This specific activity range had been covered in the first experiment reported in this paper, but under somewhat different conditions. The barley plants were transferred to corks when they were 5 days old and were allowed to grow until they were 14 days old in a nutrient solution that contained no added phosphorus. At that time the second leaf was almost fully expanded. They were then placed in the experimental solutions. Forced aeration of the nutrient solutions was employed, and the solutions were discarded and replaced every third day. The plants were allowed to remain in the experimental solutions for a total of 17 days before harvest. Table 4 shows the results obtained. The data give no evidence of radiation damage to either tops or roots at any of the P^{32} levels used. Table 4 also lists the phosphorus content of both tops and roots of these plants. There is no indication that the amount of P^{32} in the nutrient solutions affected the uptake of phosphorus by the plant either favorably or adversely during this period of growth.

TABLE 4

Effect of different levels of P^{32} in a 1 × 10^{-3} molar phosphate nutrient solution upon growth and phosphorus content of barley plants

MICROCURIES P^{32} PER LITER OF NUTRIENT SOLUTION	TOTAL LENGTH PER PLANT 3RD, 4TH, 5TH, AND 6TH LEAVES	DRY WT. (24 PLANTS)		P CONTENT OF PLANTS	
		Tops	Roots	Tops	Roots
	cm.	*gm.*	*gm.*	%	%
0	101.59	3.35	1.26	1.30	1.32
4	100.68	3.32	1.04	1.26	1.28
8	99.12	3.34	1.15	1.31	1.20
16	100.99	3.40	1.15	1.37	1.23
32	101.56	3.50	1.35	1.40	1.21
64	103.68	3.55	1.25	1.33	1.21
128	99.42	3.32	1.29	1.46	1.29
Standard Error...	1.26	0.068	0.061	0.049	0.029

Histology and morphology

At the harvest of each experiment, samples of the root tips and of the section of the stem containing the apical bud were selected for sectioning and histological examination. The results of these examinations will be reported in detail elsewhere, but it is of interest to note here that, in general, normal meristematic activity continued in the root tips and apical buds of those plants in which the leaf lengths had not been affected by radiation, and certain abnormalities appeared in the apical regions of those plants in which leaf lengths were shorter than those of the controls. Abnormalities in the apical buds appear at slightly lower specific activities of the nutrient solutions than abnormalities in the root apex. The injury to these normally rapidly growing regions appears to be a disruption of cell division and to some extent a decrease in cell elongation. The cells of the apical regions of the most severely injured plants are relatively mature, as evidenced not only by the increase in size of the individual cells, but also by a decrease in cytoplasmic density and an increase in thickness of of the cell walls. Figures 7 and 8 are photomicrographs of normal and injured root tips; figures 9 and 10, of normal and injured apical buds.

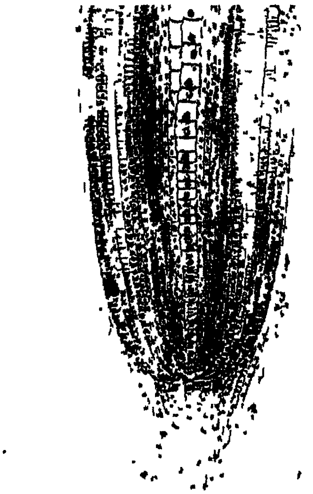


Fig 7

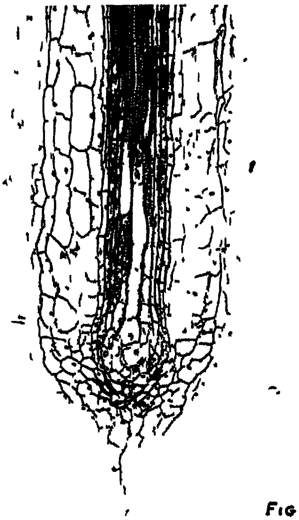
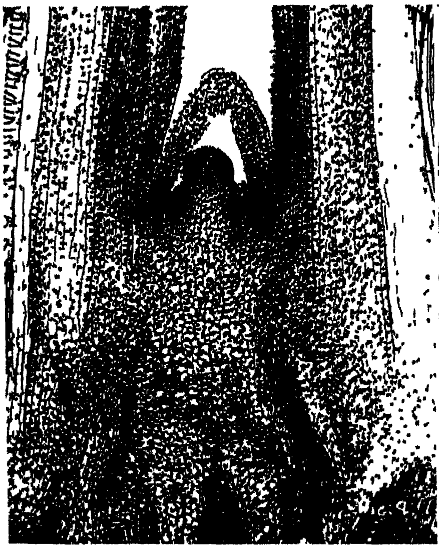


Fig 8.



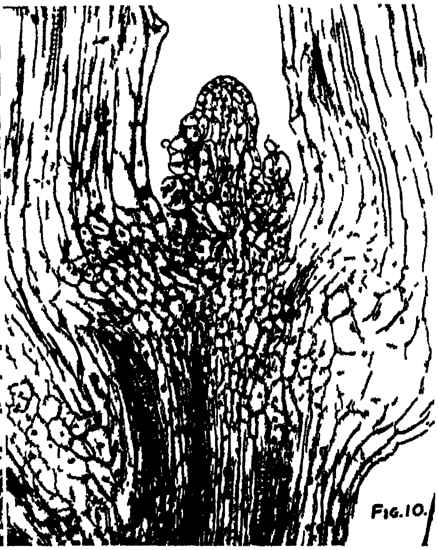


FIG. 7. ROOT TIP OF NORMAL BARLEY PLANT
FIG. 8. ROOT TIP OF BARLEY PLANT INJURED BY IRRADIATION FROM P^{32}
FIG. 9. APICAL BUD OF NORMAL BARLEY PLANT
FIG. 10. APICAL BUD OF BARLEY PLANT INJURED BY IRRADIATION FROM P^{32}

Characteristic leaf symptoms, such as those found in certain nutrient deficiencies, have not been noted in plants injured by radiation. With even the most severely damaged plants, there was no breakdown of the tissues of the older leaves. The tops stopped growing merely because new leaves failed to emerge, or if they did emerge from the sheath, failed to reach full size.

When the specific activity of the nutrient solution was very high, rather pronounced changes took place in the gross morphology of the roots. The main roots became woody and coarse; laterals were numerous, but very short and blunt. Many of the root tips were swollen and deformed. When plants were grown in nutrient solutions of somewhat lower specific activities, the roots were very nearly normal in appearance, even though the shoots were appreciably reduced in size.

DISCUSSION OF RESULTS

The exact mechanism which operates in the damage of living tissue by radiation is not yet clearly understood. Several good reviews of the subject are available (3, 4), and it is not necessary that the subject be pursued in detail in this paper. It is necessary only to know that damage to a living cell may occur when ionizing particles pass through the cell, regardless of whether the ionizing particles originate inside or outside the tissue under study.

In these studies, the ionizing particle is the electron given off in the decay of P^{32}. The mean range of this particle in tissue or water is about 3 mm., but the extreme range in these media is approximately 8 mm. Thus, any particular cell within 8 mm. of a disintegrating phosphorus atom might be traversed by the electron ejected. The leaves of the plants used in these experiments were subjected only to the ionizing particles arising from disintegration of phosphorus atoms within the leaves themselves, since the external medium was nonradioactive air, but the roots were subjected to bombardment by electrons arising from the radioactive nutrient solution in which they were immersed, as well as by electrons originating from P^{32} decay within the root.

It follows, therefore, that the greatest direct damage to the shoots may be expected under conditions that allow movement of the greatest amount of P^{32} into them. Other conditions being equal, that will happen when the specific activity of the nutrient solution is high. This is not necessarily true for the roots. Since both the P^{32} in the roots and the P^{32} of the nutrient solution may possibly cause damage to the roots, the concentrations both inside and outside the root must be considered. Therefore, not only the specific activity but also the P^{32} concentration of the nutrient solution is of potential importance.

In the experiments described, injury to both tops and roots has been associated with high P^{32}/P^{31} ratios of the nutrient solutions, rather than with simply a high P^{32} concentration. The inference is that when radioactive phosphorus is used in nutrition studies, injury to the plants is most likely under conditions that allow accumulation of the isotope within the plant. This is true even with respect to root injury. In a simple plant experiment, not reported here, plants were grown in solutions containing as much as 1 millicurie P^{32} per liter without injury to either roots or tops, when conditions were not favorable for P^{32}

accumulation within the plant. Although the radiation from the P^{32} of the nutrient solution must affect the roots to some extent, the effect appears to be minor, compared to that of the P^{32} held by the root.

The main reason for this lies in the tremendous accumulation within the active plant tissues. Representative root tips, 1 cm long, from plants grown on a 5×10^{-6} molar phosphate solution for 12 days contained 500 to 700 times as much P^{32} at harvest time as an equal volume of the original nutrient solution. No counts were made on the apical buds, but the average P^{32} content of the tops, on a volume basis, was about the same as that of the roots. Undoubtedly, the concentration in the apical bud was somewhat higher than that of the rest of the tops.

Symptoms of radiation damage appeared in the tops much more quickly than in the roots. In a series such as the one described in which treatments of 0, 2, 4, 8, 16, 32, and 64 microcuries P^{32} per liter were used in a nutrient solution 2×10^{-5} molar to phosphate, the effects of the treatment first became apparent on the highest treatment, where the second leaf appeared shorter than that of the control plants by the end of the first week. Two or three days later, it became evident that the third leaf was not developing normally on the 32-microcurie per liter treatment. In still another two days, the same effect was noticeable in the plants of the 16-microcurie per liter treatment. Thus, the higher the specific activity of the nutrient solution, the more quickly the evidence of damage appeared in the tops. In only one treatment was the leaf morphology slightly changed. The fourth leaves of the plants grown on the solution containing 8 microcuries P^{32} per liter of 2×10^{-5} molar phosphate nutrient solution was tightly furled and spikelike, and its surface was wrinkled near the base. This change in form was probably responsible for the fact that the length of this leaf was slightly greater than that of the control, although not significantly so. From observations of the behavior of the second and third leaves of plants growing on higher specific activity levels, it is believed that the fourth leaves of the plants growing on the 8-microcurie per liter treatment would have stopped growing in another day or two, and the length, therefore, would soon have been surpassed by that of the controls. If this argument is carried further, there is a possibility that the plants treated with 4 microcuries per liter might have shown injury if the experiment had been continued longer. The exact specific activity level necessary to cause detectable injury may well depend on the length of the experiment.

Both the gross appearance of the tops and the roots and the histological examination of the sections of the root tips and the apical buds lead to the conclusion that the effect of radiation has been of importance only in the regions of the plant where cells are actively dividing.

The studies reported here were carried out with nutrient solutions covering the same range of phosphate concentrations as those employed by Russell and Martin (5). Barley plants at about the same stage of growth were used in each case, but in their experiments the plants were allowed to grow in the radioactive solutions for a somewhat shorter period before harvest.

Russell and Martin reported that there was some indication that phosphate absorption by the plants from the nutrient solutions had been depressed by radiation injury. A later paper from the same laboratory (6) reported that phosphate absorption by plants from fertilizers applied to greenhouse pots was affected by the P^{32} content of the fertilizer, even when the top yield was normal. In one case, decreased utilization of fertilizer phosphate was associated with increased specific activity of the fertilizer; in another case, the reverse was found to occur.

In the experiments carried out at this laboratory, there was no evidence that the presence of radioactive phosphorus affected the absorption from the solutions. In the series in which plants were grown in a nutrient solution 2×10^{-5} molar for phosphate, radiation injury did not affect the amount of phosphorus absorbed during the growth period. In every case, the phosphate supply had been nearly exhausted by the plants during each of the 48-hour periods (table 3). This was true for all treatments. The plants grown on the 64-microcuiie per liter treatment, and which had shown severe damage for a week or more prior to harvest, absorbed just as much phosphate during each of the 48-hour periods as did the undamaged plants from the least severe treatments.

Also, the phosphate content of the plants grown in the nutrient solutions containing 1×10^{-3} moles of phosphate per liter was not affected by the P^{32} concentrations of the solutions. Table 4 shows that there was no difference in total phosphate content of either the tops of the roots or the plants, regardless of the P^{32} level of the nutrient solutions used. In none of these experiments in which plants were grown in nutrient solutions has there been any indication that radiation damage has interfered with phosphate utilization by the plant. Some preliminary studies with plants grown in greenhouse pots have indicated that under certain conditions the specific activity of a fertilizer may affect the utilization of the fertilizer phosphate. The data are contradictory and are not reported here, but they do not support the simple explanation offered by Russell and Martin, that radiation damage to roots may temporarily depress phosphate absorption from the fertilizer zone and that the absorption rate from this region may then be raised above normal when the roots recover as the P^{32} decays.

The results reported here differ from those reported by the previous workers in one other important respect. In all of these experiments the shoots were injured more severely than the roots. Furthermore, the injury developed much more slowly than in the experiments of Russell and Martin. In no case did a difference in dry weight of roots as large as 40 per cent appear in 6 days, even when the specific activity of the nutrient solution used was five to ten times that employed by those workers. In that length of time, the highest specific activities employed caused barely detectable damage to the roots and only slightly more damage to the tops.

No simple explanation can be offered for the differences between the two sets of experiments. It is likely that the environmental conditions were somewhat different in the two cases. Since there is some evidence that one step in the mechanism of radiation injury has a large temperature coefficient (3), plants grown under different environments may react differently to radiation.

The lowest level at which radiation damage has been shown corresponds to a specific activity of the nutrient solution of 5.6 millicuries per gram of P_2O_5. This appears to be safely above the level of specific activity of the radioactive fertilizer phosphates produced by the Bureau of Plant Industry, Soils, and Agricultural Engineering for distribution to the state experiment stations (usually 0.2 millicurie per gram P_2O_5). However, 5.6 millicuries per gram of P_2O_5 is not higher than might sometimes be used in nutrient culture work. In addition, work with other plants, or with barley under conditions different from those employed in these studies, may lead to finding radiation injury at lower specific activity levels. It must also be remembered that these experiments were of short duration. Plants grown on radioactive solutions for longer periods might well be damaged at lower specific activities.

Results from studies with P^{32} are not necessarily transferable to problems involving other isotopes, since the half-life, uptake, and distribution of the isotope within the plant, and the kind and energy of the radiation emitted, are all factors which will affect the amount of injury inflicted. It behooves any investigator who is using radioactive materials in experimental work with plants to recognize that radiation injury may possibly invalidate his results.

SUMMARY

Experiments are described in which young barley plants were grown in nutrient solutions containing various amounts of P^{32}. The lengths of leaves and the dry weights of tops and roots were used as the criteria of injury caused by the radioactive material. Meristematic regions of the plants were examined histologically, and photomicrographs of normal and of injured root tips and apical buds are shown.

It was found that damage to the tops was more severe than damage to the roots, and that the injury was due primarily to radiation from the P^{32} accumulated within the plant, the P^{32} which remained in the nutrient solution having relatively little effect. There was no evidence of damage to cells other than those which were in zones of active division. Absorption of phosphate from solution was not affected by radiation injury.

The lowest level at which damage was produced under the experimental conditions employed corresponds to 5.6 millicuries P^{32} per gram of P_2O_5.

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PRESSURE-CONTROL UNIT FOR USE WITH THE PRESSURE-PLATE APPARATUS FOR MEASURING MOISTURE SORPTION AND TRANSMISSION BY SOILS[1]

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Received for publication May 1, 1950

The pressure-plate apparatus as described by Richards and Fireman[2] has proved to be a very useful piece of equipment for studying moisture retention in soils in the range of 0–2000 cm. of water tension. Successful operation of the apparatus depends largely on the pressure-control unit. This unit must hold the pressure for long periods at any point in the range 0–2000 cm. water with no more than a few millimeters' variation. The pressure-control unit described by Richards and Fireman is a water tower mounted in a well below the level of the laboratory bench. Subsequently, Richards[3] described a mercury tower for pressure control which he[4] later modified by eliminating the porous disc that supports the mercury. This unit functions well, although there is a slight pulsation in the pressure; also, some might object, from a health standpoint, to having mercury exposed in the laboratory.

The pressure-control unit here described was constructed in 1947, prior to the development of the mercury-column controls. It has been much used, and the performance has been entirely satisfactory. In setting up the pressure-plate apparatus in the Rubidoux Laboratory, a well was not available. It was necessary, therefore, to mount the water towers above the bench level. Some difficulty was encountered, at first, with water syphoning back from the towers into the pressure-plate apparatus, but this was corrected with suitable traps. This paper presents a diagram and description of the unit.

MATERIALS

Figure 1 is a schematic diagram (not to scale) of the pressure-control unit. Table 1 lists the parts and shows the dimensions.

DETAILS OF CONSTRUCTION

Glass towers, parts 3 and 4, are closed by rubber stoppers. These are held in place by long bolts making an assembly similar to a water gage on a boiler.

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[1] Contribution from the U. S. Regional Salinity and Rubidoux Laboratories, U. S. Department of Agriculture, Riverside, California, in cooperation with the eleven Western States and the Territory of Hawaii. Many helpful suggestions in connection with the construction of the apparatus and in the preparation of the manuscript were made by L. A. Richards. These are gratefully acknowledged. Likewise, a word of appreciation is due Henry T. Stumpf, who assembled the unit.

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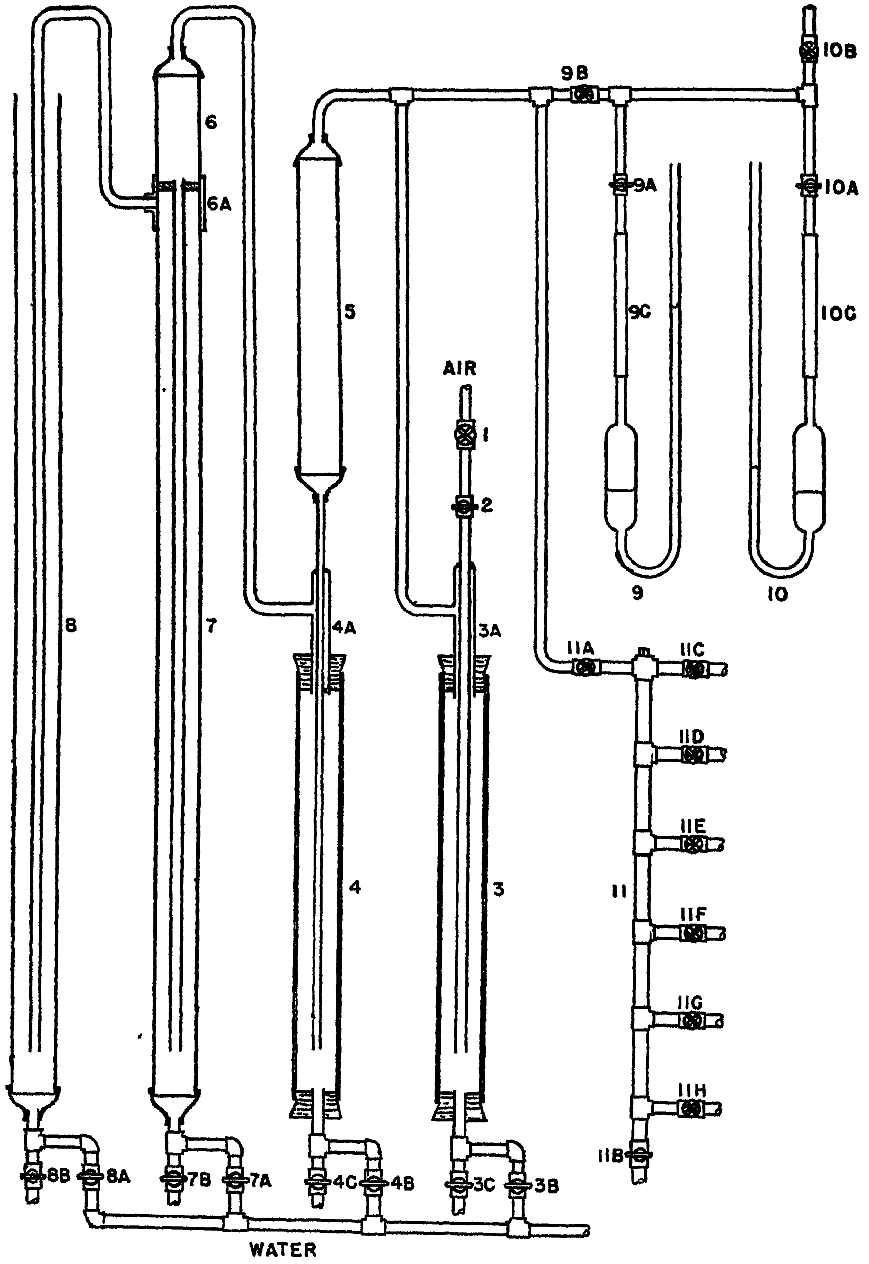

FIG. 1. SCHEMATIC DIAGRAM OF PRESSURE-CONTROL UNIT

The tees, parts 3A and 4A, are made of copper tubing. The outer shell is $\frac{1}{2}$ inch in diameter; the tube that passes through and on into the tower is $\frac{1}{4}$ inch in diameter and the side arm $\frac{3}{8}$ inch. The top of the $\frac{1}{2}$-inch tubing is closed by brazing it to the ¼-inch tubing. The lower end of the ¼-inch tube that extends nearly to the bottom of the glass tower is finished with a miter cut to facilitate bubbling. The trap, part 5, is fitted with a reducer at each end and proper fittings to connect at the bottom to ¼-inch copper tubing and at the top to ⅜-inch. Trap, part 6, is of galvanized iron, 2 feet long and 2 inches in diameter. The top is connected to ⅜-inch copper tubing by means of a reducer and the proper fittings. In the lower end of this trap, a circular plate is welded, closing the tube except for the central hole that is threaded for a ⅜-inch copper tubing fitting. The lower end of the trap is threaded on the outside and screws into the tee, part 6A.

TABLE 1

List of parts, with dimensions, for pressure-control unit

PART NUMBER	NUMBER REQUIRED	DESCRIPTION
1	1	Valves, air, brass ¼″.
2	1	Valve, needle.
3, 4	2	Tubes, glass, Pyrex 24″ long, 1″ O. D.
3A, 4A	2	Tees, copper tubing, through member ¼″ O.D.; side arm ⅜″; body ½″.
3B, 3C, 4B, 4C	4	Valves, water, brass ¼″.
5	1	Trap, galvanized iron pipe, 12″ long, 1½″ I. D. suitable reducers on each end.
6	1	Trap, galvanized iron pipe, 24″ long, 2″ I.D. reducer at top; plate welded inside at bottom with center hole threaded for ⅜″ copper tubing fitting.
6A	1	Tee, galvanized iron, 2″ by ½″ with fittings to connect ⅜″ copper tubing.
7	1	Tower, galvanized iron pipe, 32′ long; 2″ I.D.
8	1	Tower, galvanized iron pipe, 34′ long; 2″ I. D.
7A, 7B, 8A, 8B	4	Valves, water, brass ¼″.
9	1	Manometer, water, glass, side arm 165 cm. long by 8 mm. I. D.
10	1	Manometer, mercury, Pyrex glass capillary, side arm 165 cm. long by 1.5 mm. I. D.
9A, 9B, 10A, 10B	4	Valves, air, brass needle ⅛″, for use with ⅛″ galvanized iron pipe.
9C, 10C	2	Flexible rubber pressure hose connections, 2′ long by ¼″ I. D.
11	1	Manifold, pressure-plate attachments, galvanized iron pipe ½″ diameter, 4′ long, outlets spaced 8″ apart.
11A, 11B	2	Valves, air, brass, globe ⅛″.
11C to 11I	6	Valves, air, brass, angle ¼″.
12*	100–150′	Copper tubing, ⅜″ diameter.
12A*	10′	Copper tubing, ¼″ diameter.

*Not designated on figure 1.

Parts 9 and 10 are manometers for measuring the pressure applied to the pressure-plate units. Manometer 9 is for water and the indicating arm is 8 mm. inside diameter. Addition of a small quantity of methylene blue to the water in the manometer facilitates reading. Manometer 10 is for mercury, and the indicating arm is of Pyrex capillary tubing of 1.5-mm. bore. A meter stick, graduated in millimeters, on a slide that can be moved up and down, serves to measure the pressure on either manometer. The zero indicators on the meter stick should be corrected for the capillary rise, in the case of water, and depression in the case of mercury. Valves 9A, 9B, 10A, and 10B permit the use of either or both manometers.

Part 11 is the manifold to which the pressure-plate units are connected. Attachment to the pressure-plate units is made with short lengths of $\frac{3}{16}$-inch copper tubing and the proper fittings. Valves 3B, 4B, 7A, and 8A are in the water-supply lines. Valves 3C, 4C, 7B, and 8B are connected to the drain. Copper tubing $\frac{3}{8}$ inch in diameter is used for the air lines, except the through tubes of parts 3A and 4A, which are $\frac{1}{4}$-inch tubing. The manifold, part 11, and the connections to the manometers are of $\frac{1}{8}$-inch galvanized iron pipe.

OPERATION

To start the apparatus at the beginning of a run, close valves 11A to 11H. Empty towers 7 and 8. Attach the pressure-plate units, containing the moistened soil samples, to valves 11C to 11H. Put the water manometer into operation by opening valves 9A and 9B and closing 10A and 10B and adjusting the zero indicator. Fill tower 3 about half full of water. This tower serves to saturate the incoming air with water and also acts as a bubble counter that is helpful in detecting leaks but is not a part of the pressure-control system. Admit air through valve 1 and adjust the flow with needle valve 2 to a brisk bubbling rate. Admit water slowly to glass tower 4 through valve 4B until manometer 9 shows the desired pressure, usually 25 cm. water for the initial equilibrium point of the run. Open valves 11A and 11C to 11H. Readjust the flow of air with valve 2, if too rapid, to a slow steady rate. About 150–200 bubbles per minute is optimum.

After equilibrium is reached, the pressure is increased to the next higher point by admitting additional water to tower 7. For successive points, more water is admitted to tower 7, and tower 8 can be used for points above the range of tower 7 alone. For the pressures above 100 cm. water, the mercury manometer is used.

To discontinue a run and shut down the apparatus, close valves 11A and 11C to 11H and open 11B. Remove pressure-plate units, one at a time, first opening the corresponding valve and relieving the pressure in the unit. With the air still running, drain tower 8, then tower 7, in that order, and shut off air at valve 1.

THE RATE OF ELONGATION OF SUNFLOWER PLANTS AND THE FREEZING POINT OF SOIL MOISTURE IN RELATION TO PERMANENT WILT[1]

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Received for publication May 22, 1950

The wilting percentage is often taken as the lower limit of soil moisture available for plant growth. Sunflower plants are commonly used for this determination in accordance with the technic proposed by Briggs and Shantz (3) and more recently developed and described by Veihmeyer and Hendrickson (13).

Useful information relating soil moisture to plant growth may be obtained during wilting-point tests by measuring the rate of growth of the plant as the soil moisture content is reduced to the permanent wilting condition. From this type of measurement, Furr and Reeve (6) found that the rate of elongation of the central stem of the sunflower plant continuously decreases as the soil moisture is depleted from the moisture equivalent to the wilting percentage. They found that stem elongation ceased at approximately the soil moisture content they identified as the first permanent wilting percentage. The present paper reports similar measurements that have been made for a number of soils from Tulare County, California.[2]

Freezing-point measurements were made on cores of soil taken from the soil cans when the soil was deemed to be at the permanent wilting percentage (*PWP*). In addition, moisture equivalent, ⅓- and 15-atmosphere moisture retention values, and the electrical conductivity of the saturation extract were determined.

EXPERIMENTAL PROCEDURE

The soils under test were of the Hesperia, Chino, and Foster series from the San Joaquin Valley in California. Soils were sampled at 1-foot intervals to depths of 8 and 10 feet. The samples were air-dried and passed through a 2-mm. round-hole sieve before being divided into 600-gm. portions for the wilting tests. The sunflowers were of the dwarf type from an inbred line.[3] The seeds were sprouted between layers of moist cloth and were transplanted to the cans of soil when the radicle was approximately 1 cm. long. In all but a few cases, the wilting-point values given are the averages of four replicates.

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[1] Contribution from the U. S. Regional Salinity and Rubidoux Laboratories, U. S. Department of Agriculture, Riverside, California, in cooperation with the eleven Western States and the Territory of Hawaii.

[2] These soil samples were collected by the U. S. Department of the Interior, Bureau of Reclamation, and sent to the Salinity and Rubidoux Laboratories for tests relating to the range and limits of available soil moisture. The field moisture determinations were made by the Bureau of Reclamation.

[3] Obtained from G. O. Baker, University of Idaho.

One-half gram of superphosphate was mixed with the soil in each can, and the water used for irrigation contained 2 me. per liter of KNO_3. At times, later in the experiment, $Ca(NO_3)_2$ and NH_4NO_3 were substituted for part of the KNO_3. Centrally punched lids and cotton plugs were used to close the tops of the cans to prevent vapor loss. The cotton plugs were installed at the time of the final irrigation. A humid chamber was used to check the plants for permanent wilting. Plants were judged to be at permanent wilt if they failed to recover after a period, usually 18 hours, in the humid chamber.

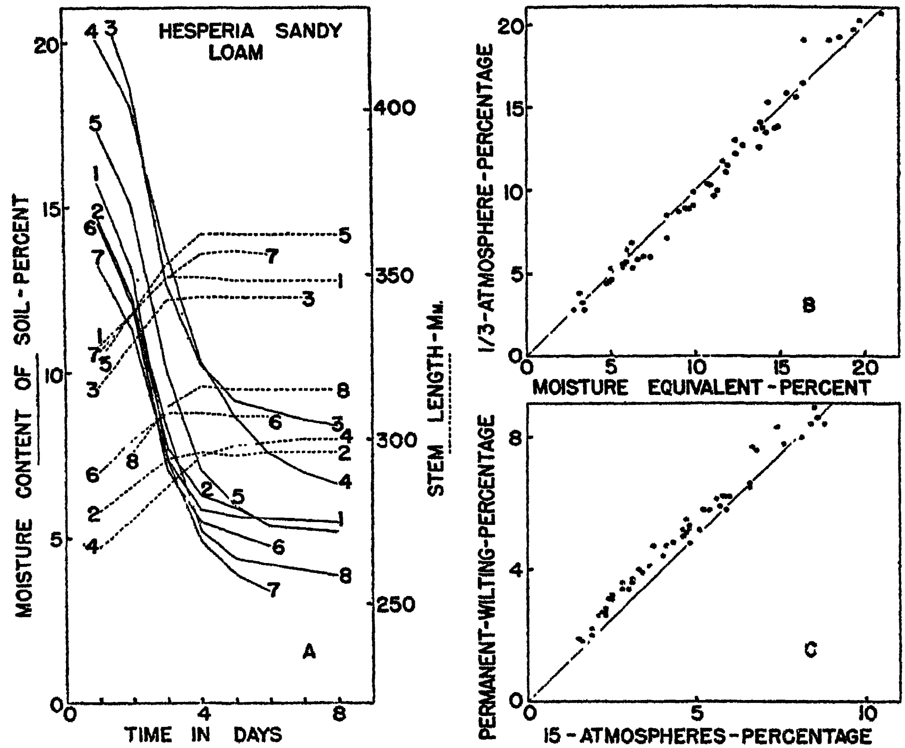

Fig. 1. A- Change in Soil Moisture Content and in Sunflower Stem Length with Time for Hesperia Sandy Lome. B- Relation of $\frac{1}{3}$- Atmosphere Percentage to the Moisture Equivalent. C- Relation of the 15- Atmosphere Percentage to the Permanent Wilting Percentage.

The 45° lines are drawn in for reference.

The gross weights of the cans and the heights of the plants were measured at approximately the same hour each day after the final irrigation. Two soil cores, 5 cm. long and 1.9 cm. in diameter, were taken for freezing, a core-handling procedure and a freezing technic previously described (8, 9) being used. Separate subsamples of soil were used for the moisture equivalent and the $\frac{1}{3}$- and 15-atmosphere percentage determinations according to the procedures given by Briggs and McLane (2) and Richards and Weaver (7).

EXPERIMENTAL RESULTS

The change of soil moisture and of sunflower stem length with time is illustrated in figure 1A for Hesperia sandy loam. The curves represent the averages for the replicates, and the numbers on the curves indicate, in feet, the depth interval for the samples. The curves terminate at the time when the plant was deemed to be at the permanent wilting percentage. It is seen that moisture extraction (transpiration) takes place at a gradually decreasing rate and that stem elongation stopped some days in advance of attainment of the final moisture content. The curves showing change in stem length with time are essentially similar to the curves obtained by Wadleigh and Gauch (15) for change in length of cotton leaves with time during an irrigation cycle.

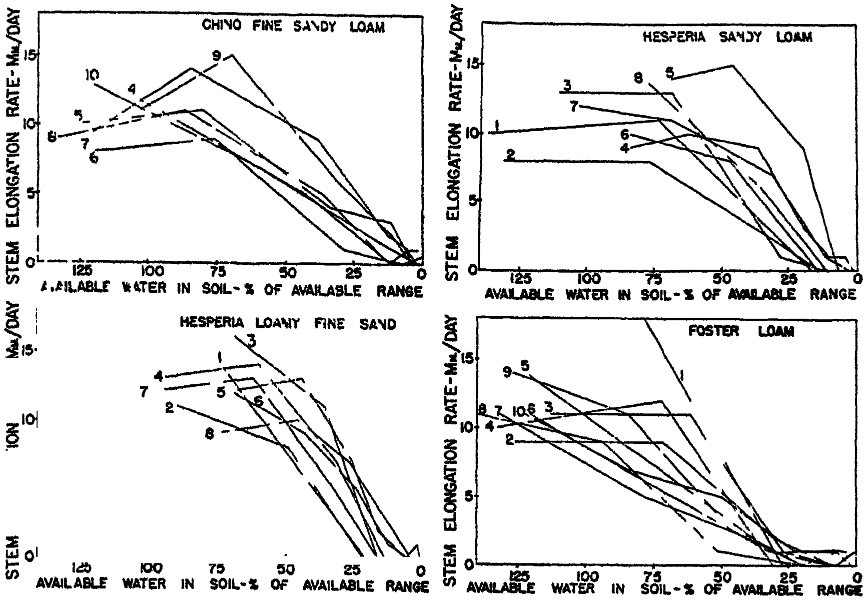

FIG. 2 TIME RATE OF ELONGATION OF SUNFLOWER STEM IN RELATION TO PERCENTAGE OF AVAILABLE WATER REMAINING IN SOIL

Each curve represents average data for four replicates The soil samples were collected from successive depth intervals of 1 foot in the profile, and the numbers on the curves indicate the sample depth

The explanation is somewhat uncertain for the downward curvature and point of inflection occurring in the moisture content curves during the first 2 days. The plants sometimes showed wilting symptoms before irrigations prior to the final irrigation. Apparently, a day or two is required after a period of moisture stress for the young plants to re-attain maximum transpiration rates, as shown by soil moisture depletion rates in figure 1A and maximum growth rates in figure 2.

The curves in figure 2 show graphically the relation of the stem elongation rate to the percentage of available water remaining in the soil. This moisture index was calculated from the relation $\frac{(Pw - PWP)}{(FC - PWP)}$ 100. This gives the percentage of available water remaining in the soil at the time when the moisture percentage of the soil is Pw. The field capacity values (FC) were obtained from field samples taken by the Bureau of Reclamation, U. S. Department of the Interior. Each curve represents the average for four replicates. The soil moisture value for each experimental point on the curves is the average value for the time interval between two weighings and is plotted against the average stem elongation rate for the same interval.

TABLE 1

Data related to the condition of soil moisture at permanent wilting of sunflowers

ACC. NO.	DEPTH	PWP	FAP	ΔT_s	12.05 × ΔT_s	OP*
	ft.	%	%	°C.	*atmos.*	*atmos.*
			Hesperia sandy loam			
3310	0–1	4.0	3.3	1.78	21.4	4.7
3311	1–2	3.5	2.8	1.69	20.4	4.8
3312	2–3	3.7	3.1	1.72	20.7	4.9
3313	3–4	2.8	2.3	1.68	20.2	5.4
3314	4–5	3.4	2.8	1.42	17.1	5.7
3315	5–6	3.6	3.1	1.43	17.2	4.1
3316	6–7	3.1	2.5	1.44	17.4	5.7
3317	7–8	2.2	1.9	1.39	16.7	7.2
			Hesperia loamy fine sand			
3318	0–1	5.3	4.8	1.24	14.9	5.2
3319	1–2	7.6	6.7	1.24	14.9	3.6
3320	2–3	7.6	6.8	1.24	14.9	3.0
3321	3–4	8.3	7.4	0.83	10.0	3.1
3322	4–5	8.4	8.4	1.07	12.9	3.1
3323	5–6	8.9	8.5	1.26	15.2	3.4
3324	6–7	8.6	8.6	1.52	18.3	3.3
3325	7–8	8.0	8.1	1.43	17.2	3.8
			Chino fine sandy loam			
3326	0–1	4.7	3.7	0.97	11.7	5.4
3327	1–2	3.2	2.5	1.27	15.3	5.2
3328	2–3	3.1	2.4	1.24	14.9	4.9
3329	3–4	2.7	2.2	1.57	18.9	6.8
3330	4–5	2.6	2.1	1.52	18.3	6.6
3331	5–6	2.6	2.3	1.54	18.6	7.1
3332	6–7	2.0	1.9	1.58	19.0	10.1
3333	7–8	1.8	1.6	1.59	19.2	10.2
3334	8–9	1.9	1.5	1.53	18.4	9.9
3335	9–10	2.7	2.3	1.54	18.6	7.3

* Estimated value of the osmotic pressure of the soil solution at permanent wilt. See text for method of calculation.

TABLE 1—*cont'd.*

Data related to the condition of soil moisture at permanent wilting of sunflowers

ACC. NO.	DEPTH	PWP	FAP	ΔT_0	$12.05 \times \Delta T_0$	OP*
	ft.	%	%	°C.	*atmos.*	*atmos.*
			Hesperia sandy loam			
3336	0–1	5.5	4.7	1.47	17.7	4.8
3337	1–2	5.2	4.8	1.58	19.0	4.7
3338	2–3	8.4	8.8	1.73	20.8	3.4
3339	3–4	6.6	6.6	1.75	21.1	3.6
3340	4–5	5.2	5.1	1.76	21.2	4.8
3341	5–6	4.8	4.8	1.82	21.9	4.2
3342	6–7	3.4	3.0	1.71	20.6	7.3
3343	7–8	3.9	3.4	1.87	22.5	7.8
			Hesperia loamy fine sand			
3344	0–1	5.8	5.4	1.67	20.1	4.7
3345	1–2	6.2	5.8	1.58	19.0	3.8
3346	2–3	6.6	6.6	1.80	21.7	3.8
3347	3–4	6.2	5.8	1.58	19.0	3.8
3348	4–5	6.2	6.0	1.69	20.4	4.2
3349	5–6	6.5	6.6	1.68	20.2	4.0
3350	6–7	5.9	5.7	1.74	21.0	4.1
3351	7–8	4.4	4.0	1.65	19.9	5.8
			Foster loam			
3352	0–1	7.8	7.6	1.35	16.3	4.0
3353	1–2	6.1	5.6	1.57	18.9	4.1
3354	2–3	5.1	4.6	1.84	22.2	4.9
3355	3–4	4.8	4.3	1.86	22.4	6.1
3356	4–5	4.1	3.6	1.84	22.2	5.8
3357	5–6	5.2	4.6	1.59	19.2	5.4
3358	6–7	5.8	5.9	1.50	18.1	5.0
3359	7–8	5.8	5.2	1.42	17.1	4.4
3360	8–9	5.1	4.7	1.59	19.2	4.3
3361	9–10	4.7	4.1	1.21	14.6	5.3
Average.		5.0	4.6	1.53	18.5	5.2

* Estimated value of the osmotic pressure of the soil solution at permanent wilt. See text for method of calculation.

Furr and Reeve (6) found that the daily elongation rate of sunflower stems decreased approximately linearly with time as the soil moisture was depleted during a wilting test. Various factors influence the conventional wilting point test. Some of these are the rapid depletion of available water and the diurnal changes in elongation rate, which are due to uncontrolled, periodically varying environmental conditions. Because of this, it does not seem worthwhile to investigate mathematically the shape of the curves in figure 2. It is quite clear from the curves, however, that the elongation rate of sunflowers is markedly decreased before half of the so-called available water is used and drops to zero before the permanent wilting percentage is attained. Curves substantially similar to those in figure 2 are obtained if the stem elongation rate is plotted against available water in the soil when the ⅓-atmosphere percentage instead of field capacity is used as the 100 per cent point.

The relation of the ⅓-atmosphere percentage to the moisture equivalent is shown graphically in figure 1B. In accordance with the conclusion of Richards and Weaver (7), these quantities are closely related, but neither is very usefully related to field capacity for coarse textured soils such as are represented by these samples.

The permanent wilting percentages for each soil profile are given in table 1 along with corresponding 15-atmosphere percentage values and observed freezing-point depression values. The average standard error among replicates for permanent wilting percentage values for all of the samples was 0.067 per cent. The relation of the permanent wilting percentage to the 15-atmosphere percentage (*FAP*) is shown graphically in figure 1C. This relation may be represented by the linear equation: $PWP = 0.66 + 0.943 \times FAP$. *PWP* may be calculated from the equation with a standard error of estimate of 0.27 per cent and a standard error of the regression coefficient of 0.019 for this group of 52 soils.

Freezing-point measurements on soil moisture in the wilting range have been made by a number of investigators (1, 9, 10, 12, 13), and freezing-point depression values are reported to vary from 0.83 to 3.56°C. To approximate soil-moisture-stress values for comparison with the 15-atmosphere determination, the observed freezing point depression values given in table 1 have been multiplied by 12.05[4].

In most cases, the ΔT_0 values given in table 1 represent the average for eight cores, two from each can, taken at the termination of the wilting test. The sampling tube used caused a minimum of disturbance of the soil structure. The frequency distribution for the freezing measurements at wilting is indicated by the following arrangement of the data.

NUMBER OF SAMPLES	ΔT_0 RANGE °C.	$12.05 \times \Delta T_0$ ATMOS.	% OF ALL SAMPLES
3	0.830–1.212	10.0–14.6	6
11	1.220–1.494	14.7–18.0	23
34	1.502–1.876	18.1–22.5	71

The hyperbolic relation between *Pw* and ΔT_0 for any one soil is indicated by an examination of individual pairs of data. For the four replicates of each sample the highest moisture content at the permanent wilting condition usually corresponded to the lowest value for ΔT_0. For example, the maximum and minimum values of ΔT_0 and 12.05 ΔT_0 with individually corresponding values of *PWP* for Foster loam replicates are given in table 2. The average difference between maximum and minimum *PWP* values for the replicates of these samples was 0.13, and on the average this corresponded to a ΔT_0 difference of 0.25°C., which corresponds to 3 atmospheres of equivalent soil-moisture stress.

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[4] Interpretation of freezing-point data in terms of free energy or soil moisture stress is complicated by the fact that a correction should be subtracted from the observed freezing-point depression values ΔT_0 before standard formulas (5, 11) for converting to free energy can be used. The procedure for evaluating this correction has not been clearly established Consequently, multiplying the observed freezing point depression by 12.05 gives only an approximate value for the equivalent soil-moisture stress.

At the conclusion of the wilting tests, the oven-dried soil was examined for salinity and the osmotic pressure of the soil solution at the wilting percentage was estimated. The soils were made up to a saturated paste by stirring with water, and the saturation percentage (*SP*) and the electrical conductivity of the saturation extract ($EC_e \times 10_e$) were determined. Multiplying the latter by *SP*/*PWP* approximates the conductivity of the soil solution at the wilting percentage and this in turn may be converted to osmotic pressure by use of the conversion formula $OP = 0.321 \times (EC_e \times 10^3)^{1.065}$ recently obtained by Campbell, Richards, and Bower (4) for soil solutions. This calculation assumes the solubility and ionization of the soil salts to be independent of the soil moisture content. Oven-drying also appreciably alters the solubility of some soil constituents, but as these soils were nongypsiferous, the above procedure may give a reasonably reliable estimate of the osmotic pressure of the soil solution at permanent wilt. The values thus obtained are listed in the last column of table 1.

TABLE 2

High and low free-ing-point depression values and corresponding permanent wilting percentage values for the Foster loam profile

SOIL ACC. NUMBER	LOW VALUE		PWP	HIGH VALUE		PWP
	ΔT_0	12.05 ΔT_0		ΔT_0	12.05 ΔT_0	
	°C.	*atmos.*	%	°C.	*atmos.*	%
3352	1.295	15.6	7.72	1.448	17.5	7.67
3353	1.467	17.7	6.23	1.653	19.9	6.16
3354	1.732	20.9	5.06	1.945	23.4	5.01
3355	1.601	19.3	4.96	1.981	23.9	4.66
3356	1.607	19.4	4.26	2.030	24.4	4.03
3357	1.518	18.3	5.11	1.634	19.7	5.10
3358	1.244	15.0	5.94	1.722	20.8	5.78
3359	1.286	15.5	5.90	1.518	18.3	5.76
3360	1.461	17.6	5.09	1.652	19.9	4.91
3361	1.125	13.6	5.04	1.285	15.5	4.89
Average	1.434	17.3	5.53	1.687	20.3	5.40
Difference between averaged values....				0.253	3.0	0.13

Since the texture range represented by the samples is not large, it is of interest to consider average values for the columns in table 1. The 15-atmosphere percentage is 0.4 per cent lower than the permanent wilting percentage. It may be inferred from this that on the average the soil moisture tension at permanent wilting is less than 15 atmospheres. The average calculated soil-moisture stress minus the estimated osmotic pressure is seen to be 13.3 atmospheres.

It was deemed advisable to test whether significant variability occurred between the two soil cores subjected to freezing from the various containers of soil over and above any variance in freezing data induced by the specific nature of the soils themselves. To this end, the data were reduced with a segregation of error variances analogous to the procedure used for split-plot experiments. (15). The analysis given in table 3 shows that there was no significant difference between two values for the freezing-point depression of the cores taken from each soil container and that this comparison was completely independent of the nature of the soil samples studied.

TABLE 3

Analysis of variance of the freezing data

SOURCE OF VARIATION	SUMS OF SQUARES	DEGREES OF FREEDOM	VARIANCE
Total	14.057,064	319	.044066
Soils	10.395,156	39	.266542**
Replicates	0.362,052	3	.120684
Error 1	2.942,168	117	.025147
Freezings	0.003,342	1	.003342
Freezing × Soils	0.069,913	39	.001793
Error 2	0.284,433	120	.002370

** Significant at the 1 per cent level.

SUMMARY

Permanent wilting percentage, moisture equivalent, 1/3-atmosphere percentage, and 15-atmosphere percentage values were measured on 52 soil samples representing six profiles of three soil series from the San Joaquin Valley, California. The time rate of elongation of sunflower stems was measured in relation to soil-moisture depletion following the final irrigation, and the freezing-point depression was measured on soil cores at the permanent wilting percentage.

The rate of moisture depletion (transpiration) decreased gradually as the condition of permanent wilt was approached. The time rate of stem elongation of sunflowers was markedly reduced before half of the available water was depleted. The rate of stem elongation dropped to zero during extraction of the last quarter of the available soil water and before attainment of the permanent wilting percentage.

The relation between the permanent wilting percentage (*PWP*) and the 15-atmosphere percentage (*FAP*) for these soils was found to be $PWP = 0.66 + 0.943 \times FAP$.

The average uncorrected freezing-point depression at wilting for this group

of 52 soil samples was 1.53°C. Freezing-point values ranged from 0.829 to 1.876, and 71 per cent of the values were in the range 1.494 to 1.876°C.

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PHOSPHATES IN CALCAREOUS ARIZONA SOILS: I. SOLUBILITIES OF NATIVE PHOSPHATES AND FIXATION OF ADDED PHOSPHATES

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Received for publication April 17, 1950

Although calcareous Arizona soils contain an adequate supply of native phosphorus to produce crops for many centuries under the present cropping system, most soils show crop-yield response to phosphate fertilizer applications. The fact that the abundance of this natural resource has been known for many years, yet it still remains locked from the reach of the plant, is a challenge to the soil investigator. Some of the factors contributing to the low "availability" of native phosphorus have been briefly explored, but for the most part, the mechanisms responsible for fixation in calcareous soils are not known.

Native phosphates in irrigated Arizona soils are characteristically more readily soluble in weak or dilute acids and neutral salt solutions than are phosphates of acid soils (10). Indeed, these solutions make such large quantities of phosphorus soluble they are of little value for use in a method designed to predict availability to plants. Carbonic acid, formed by bubbling CO_2 into water, has been used with considerable success, however, for determining "availability" of phosphates in soils (9, 11). The very mild acid reaction is thought to be similar to that surrounding the plant root. Some investigators assert that the "availability" of phosphorus of calcareous soils can best the evaluated by extraction with water (1, 2).

A certain amount of phosphorus added to calcareous Arizona soils becomes unavailable to plants and is referred to as "fixed." Soluble phosphorus may be fixed in organic as well as inorganic forms. Inorganic fixation may be due to absorption reactions or precipitation. In Arizona soils, calcium is considered to unite with soluble phosphorus to form phosphates of varying degree of solubility (10, 11). The more insoluble phosphates appear to possess characteristics similar to carbonatoapatite (8, 9). For the most part, the solubility of phosphorus added to calcareous soils has not been clearly characterized. Such a characterization is essential as a basis for determining a long-time fertilizer program.

Soluble soil phosphorus also may be fixed by the soil microflora in the form of microbial tissues and products, the availability of which is probably very low. Since it is established that all microbial cells need phosphorus for their persistence, the quantity fixed in the soil in organic form is related to the number, kind, and activity of the microorganisms. The extent of microbial fixation and mineralization is expected to vary with different soil types and is determined by the circumstances under which the soils exist. Incubation of soils in absence of a readily available energy source may not be expected to affect the phosphorus status of the soil to an appreciable extent as shown by investigations with calcareous soils of Idaho (8) and Washington (13). The extent of fixation by microorganisms in soils in presence of available energy sources is not well known. Moreover, the rate of mineralization or liberation of biologically fixed phosphorus for plant use has not been clearly shown.

The objectives of the investigation reported here are to determine, first, the relationship between the availability of native phosphates to plants and the solubility of the phsophates in CO_2-charged water and in water alone, a relationship, knowledge of which appears to be particularly desirable because field data indicate that the amount of phosphorus available under wet conditions may be quite different from that under drier circumstances; second, the extent to which soluble phosphorus added to calcareous Arizona soils is fixed or absorbed as measured by its susceptibility to extraction with water and CO_2-charged water; and third, fixation and mineralization of soluble phosphorus in soil solution in presence of available carbon.

MATERIALS AND METHODS

The source of soils used in this and following investigations are shown in table 1. Representative samples were taken from three agricultural valleys: Salt River, Safford, and Santa Cruz. Most of the soils were planted to alfalfa at the time of collection. Only a few showed no response in the field to phosphate fertilization.

Total extractable, inorganic, and organic phosphorus in the soils was determined according to the procedure outlined by Pearson (12).

Inorganic phosphorus of water and of CO_2 extracts was determined by the colorimetric procedure of Dickman and Bray (4) with an Evelyn photoelectric colorimeter fitted with filter 660.

Carbon dioxide extractions were made by the method of McGeorge (10).

Carbonates were determined with the Emerson (6, pp. 110–112) method and apparatus.

"Active" calcium was determined by the method of Drouineau (5); and total calcium, by Chapman's method (3).

Phosphorus of plants was determined in nitric acid solution according to the vanadate method (7), after ignition in a furnace at 500°C.

Saturated soil pastes were prepared according to the procedure suggested by the U. S. Regional Salinity Laboratory.[1]

Absorption of soluble phosphorus by calcareous soils was studied by adding phosphorus as KH_2PO_4 in solution to four soils at the rate of 100 and 250 pounds P_2O_5 per acre (6-inch layer) and allowing these to stand 48 hours before extraction with CO_2 and 1:5 water. The phosphate solution was sufficient to bring the soil moisture to saturation. The soils were divided into two groups. One set was allowed to air-dry 48 hours before extraction, and the other set was extracted wet after standing for a similar time. Some of the mositure was allowed to escape from the wet sample to avoid anaerobic conditions. To allow the phosphate to approach equilibrium, the water was kept in contact with the soil for 2 hours before filtration. Longer periods of contact failed to put significantly more phosphorus into solution. Soils 4a and 7a are low in phosphorus whereas soils 6, 14, and 16a are well supplied with extractable phosphorus.

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[1] Richard, L. A. 1947 Diagnosis and improvement of saline and alkali soils. Mimeo. Handb., Riverside, Calif.

TABLE 1

Source of soil samples

SOIL NUMBER	SOIL TYPE	DEPTH	CROP	LOCATION	RANCH
		inches			
1a	Mohave sandy loam	0–6	Alfalfa	Salt River Valley	Bartlet—Heard
1b		10–16	Alfalfa	Salt River Valley	Bartlet—Heard
2	Mohave loam	0–6	Alfalfa	Salt River Valley	Freestone, Blain
3a	Mohave clay loam	0–6	Alfalfa	Salt River Valley	Goodyear farm
3b		10–16	Alfalfa	Salt River Valley	Goodyear farm
4a	McClellan loam	0–6	Alfalfa	Salt River Valley	Burns, N. R.
4b		10–16	Alfalfa	Salt River Valley	Burns, N. R.
5a		0–6	Alfalfa	Salt River Valley	Fenneley Ranch
5b		10–16	Alfalfa	Salt River Valley	Fenneley Ranch
6		0–6	Alfalfa	Salt River Valley	Cowden, Ray
7a		0–6	Alfalfa	Salt River Valley	Tatum, George
7b		10–16	Alfalfa	Salt River Valley	Tatum, George
8	McClellan silty clay loam	0–6	Barley	Salt River Valley	Harri, Chris
9	Laveen clay loam	0–6	Fallow	Salt River Valley	U. of A. Mesa Farm
10		0–6	Virgin	Salt River Valley	U. of A. Mesa Farm
11	Sunrise clay loam	0–6	Alfalfa	Salt River Valley	Painter, John
12a		0–6	Alfalfa	Salt River Valley	Price, Arthur
12b		10–16	Alfalfa	Salt River Valley	Price, Arthur
13	Pima silt loam	0–6	Virgin	Salt River Valley	Indian Reservation
14	Pima clay loam	0–6	Alfalfa	Safford Valley	Marshall—Pima
15	Cajon sandy loam	0–6	Virgin	Safford Valley	U. of A. Farm—Safford
16a	Pima clay loam	0–6	Virgin	Santa Cruz Valley	Rogers—Tucson
16b		6–12	Virgin	Santa Cruz Valley	Rogers—Tucson
17	Gila loam	0–6	Alfalfa	Santa Cruz Valley	U. of A. Farm—Tucson
18	Gila silty clay	0–6	Alfalfa	Santa Cruz Valley	U. of A. Farm—Tucson
19	Gila clay	0–6	Alfalfa	Santa Cruz Valley	U. of A. Farm—Tucson
20	Gila silt loam	0–6	Alfalfa	Santa Cruz Valley	,U. of A. Farm—Tucson

RESULTS

The total acid- and alkali-soluble phosphorus shown in table 2 represents the amount extracted by repeated treatment with warm N HCl solution followed by hot 0.5 N NH_4OH solution according to Pearson (12). Such treatment probably does not remove all the phosphorus from the soil minerals. The amount removed, more than 80 per cent of the total, nevertheless represents that portion of the phosphorus that would be of potential value to crops either in the near or distant future.

The data in table 2 show that surface soils are higher in total extractable, CO_2 soluble, and water-soluble phosphorus than are subsurface soils. The greatest amount of phosphorus was found in the CO_2 extracts and the least in the saturated paste extracts. Those soils having the greatest amount of CO_2 soluble phosphorus also had the greatest amount of water-soluble phosphorus. Only soils with 7 or more ppm. inorganic PO_4 in the CO_2 extracts were found to have inorganic phosphorus in the saturated paste and 1:2 water extracts. The history

TABLE 2

Carbonic acid and water-soluble phosphates of some Arizona soils

Expressed as ppm. soil

SOIL NUMBER	TOTAL ACID- AND ALKALI-SOLUBLE PHOSPHORUS	CO_2-SOLUBLE PO_4		1:2 SOIL-WATER-EXTRACTED PO_4, IGNITED	SATURATED-PASTE-EXTRACTED PO_4, IGNITED	CARBONATE Ca × 10^3	"ACTIVE" Ca × 10^3	pH OF SOIL PASTE
		Not ignited	Ignited					
			Surface soils, 0-6 inches					
1a	459	1.90	3.86	0.74	0.41	10.7	4.4	8.20
2	331	0.98	2.14	0.77	0.33	9.0	4.6	8.50
3a	732	2.30	8.46	—	0.41	9.7	5.5	8.10
4a	416	1.16	4.29	0.72	0.61	44.7	10.6	8.05
5a	300	1.16	2.08	0.43	0.16	Trace	4.4	8.00
6	602	19.67	21.33	2.13	0.84	58.0	15.5	8.00
7a	527	6.13	9.20	0.51	0.43	49.6	9.9	8.20
8	690	3.00	3.80	0.61	0.33	27.9	7.7	8.30
9	896	22.98	26.80	—	1.77	83.8	12.9	8.25
10	760	9.20	15.02	—	0.67	77.8	17.3	7.65
11	523	3.24	5.52	0.60	0.31	95.4	32.3	8.55
12a	846	1.75	7.35	0.54	0.54	104.7	25.2	8.40
13	1255	8.83	10.90	0.20	0.11	73.1	15.3	7.90
14	780	7.48	9.14	1.87	0.90	—	—	8.05
15	500	14.70	18.39	1.84	0.34	16.3	5.9	8.05
16a	1480	39.80	47.00	—	—	1.6	6.9	8.10
18	760	3.48	10.66	0.95	0.60	24.5	12.3	8.35
19	853	16.48	24.52	0.34	0.37	41.1	16.2	8.55
20	650	4.60	8.15	0.42	Nil	—	—	8.20
			Subsurface soils, 10-16 inches					
3b	524	1.53	2.45	0.34	0.23	11.8	5.5	8.00
4b	349	0.86	1.16	0.58	0.23	45.6	10.9	8.10
5b	187	0.86	1.53	0.53	0.19	1.1	4.1	7.60
7b	357	2.15	4.90	0.24	0.15	88.6	18.0	8.15
12b	697	1.10	4.75	0.51	0.51	124.9	28.4	8.20

of samples 6, 9, and 19 shows that phosphate fertilizers had been added to these soils at one time. This is responsible for their favorable supply of water-soluble phosphorus. The other soil samples, 13, 14, 15, and 16a, that appear to have an adequate supply of phosphorus, are either virgin or have been brought under cultivation only very recently. Ignited extracts were higher in phosphates than extracts not ignited, indicating the presence of water-soluble organic phosphorus. The quantity of this was considerable. In fact, water-soluble organic phosphorus was the only source of this element found in water extracts from soils low in phosphorus.

Calcium-phosphorus relationships

Calcium is considered to be one of the most likely factors controlling the availability of phosphorus to plants in irrigated Arizona soils. For this reason the calcium-phosphorus relationships of some soils were studied to determine the influence of the presence of soil calcium on phosphorus solubility. "Active" calcium as distinguished from total carbonate calcium in this investigation represents the amount of soil calcium that reacts with 0.2 *N* ammonium oxalate. The degree of fineness and other physical properties of the carbonates are believed to control the amount of "active" calcium and consequently may have a closer relationship to the "availability" or solubility of soil phosphorus than the total amount. Data in table 2 showing the calcium content of some Arizona surface or subsurface soils fail to indicate that high values of CO_2-soluble phosphate are necessarily correlated with low values of carbonate calcium or "active" calcium. Furthermore, a low ratio of "active" calcium to carbonate calcium was not always associated with high solubility of phosphorus though the ratio ranged from 0 to 6.8.

TABLE 3

Calcium-phosphorus relationships in virgin Pima clay loam (16a) at various depths

DEPTH	TOTAL P	CO_2-SOLUBLE P	"ACTIVE" Ca	CARBONATE Ca	"ACTIVE" Ca/CO_2-SOLUBLE P × 100	CARBONATE Ca/TOTAL P
inches	*ppm*	*ppm*	*ppm.*	*ppm*		
0–1½	1500	16.25	5,200	400	3.2	0.27
1½–3	1408	19.90	6,400	1,100	3.2	0.78
3–6	1512	17.50	8,600	2,100	4.9	1.39
6–12	1156	3.50	13,800	29,900	39.4	25.86
12–20	1060	1.56	14,800	41,100	94.9	38.77

On the other hand, a relationship between calcium and phosphorus was apparent within a single soil profile. A lower solubility of phosphates in subsoil samples as compared to surface samples of a given soil was associated with a larger quantity of both "active" and carbonate calcium. This same relationship is also clearly demonstrated in virgin Pima clay loam at several depths (table 3). The "active" calcium to carbonate calcium increased with depth, whereas the CO_2-soluble phosphorus decreased. The significance of this relationship is difficult to ascertain in view of the variable results between comparable horizons of different soils.

Solubility of phosphates

A comprehensible study on the water solubility of phosphorus at different soil-water ratios was thought to be desirable to learn more about the water-soluble characteristics of native phosphorus and to determine the relationship between solubility in water and availability to plants. The influence of water dilution on phsophorus solubility of calcareous soils that respond but little to phosphorus applications is typified by the data in figure 1. Increasing amounts of phosphorus were released as the ratio was raised from 1:1 to 1:20. The virgin Pima clay loam, soil 16, released more than 20 times as much phosphorus at a 1:20 ratio as at the narrower ratio of 1:1. The solubility of the organic phosphosur, shown by the difference between the inorganic and total extractable phosphorus, also increased somewhat at the higher dilutions.

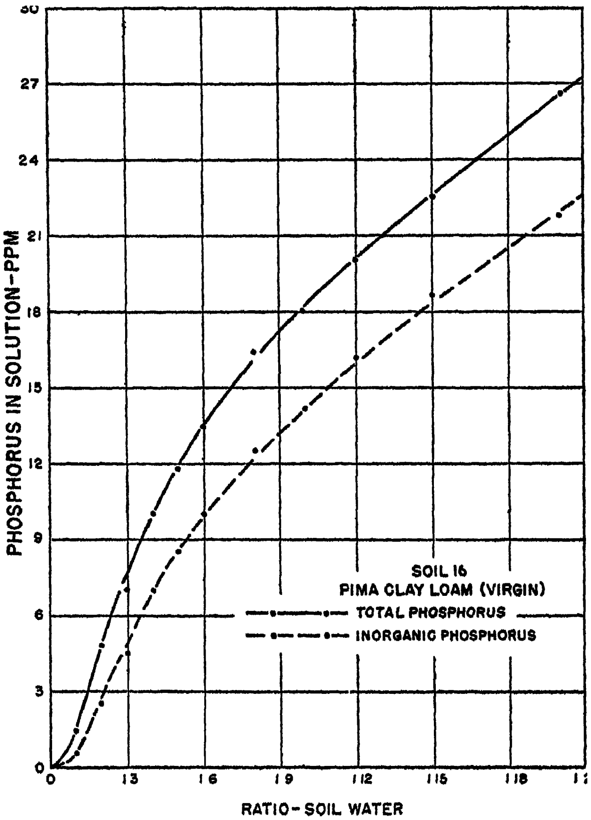

FIG. 1. SOLUBILITY OF PHOSPHORUS IN AQUEOUS EXTRACTS OF VIRGIN PIMA CLAY LOAM AT DIFFERENT RATIOS OF SOIL TO WATER

The influence of water dilution on the solubility of the phosphates of calcareous soils 1a and 7a, low in "available" phosphorus, is shown in figure 2. Unlike the soils better supplied with soluble phosphorus, these soils exhibited a maximum phosphorus solubility before a dilution of 1:20 was reached. Even the inorganic phosphorus of Mohave sandy loam approached a constant value at a ratio much below 1:20. This characteristic leveling off in solubility at the lower dilutions appears to distinguish the phosphorus-poor from the phosphorus-rich soils.

Plants in the field continually remove phosphorus from the soil solution. Thus the phosphorus-supplying power of a soil may be evaluated to a certain extent by the characteristic rate of replenishment of phosphorus to the soil solution. The ability of a soil to release phosphorus upon repeated extraction with water at a 1:5 ratio was studied by placing 100-gm. samples of soil in bottles with 500 ml. of distilled water, shaking for 2 hours in and end-over-end mixer, and filtering immediately in a Büchner funnel with vacuum. Total phosphorus and inorganic phosphorus were determined on the clear filtrate. After the first extraction, one sample was kept wet continuously during the time of extraction, whereas a duplicate sample was allowed to air-dry completely between extractions. Since experiments of this nature are possible only with soils having fair amounts of phosphorus, soils 14 and 16a were selected. The rate of release is shown in table 4.

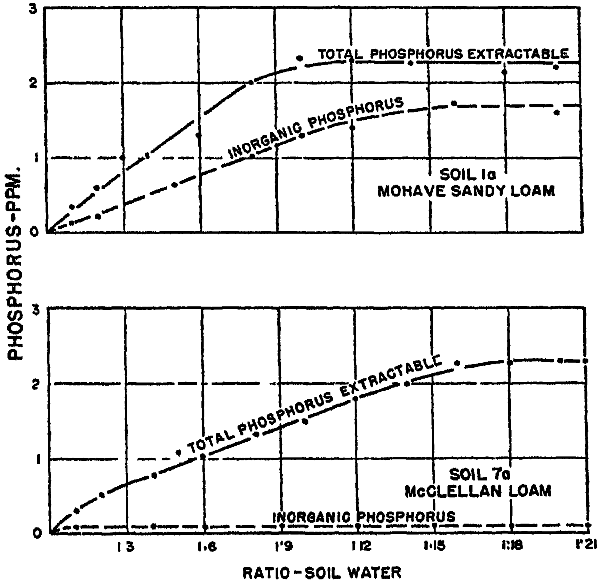

FIG. 2. SOLUBILITY OF PHOSPHORUS IN AQUEOUS EXTRACTS OF CULTIVATED MOHAVE SANDY LOAM AND McCLELLAN LOAM AT DIFFERENT RATIOS OF SOIL TO WATER.

There was very little difference in the quantity of phosphorus released as a result of the wetting and drying treatment as compared to keeping the soils wet continuously. Fixation as a result of drying did not appear as a factor in the quantity of phosphorus liberated. The continual release of phosphorus of non-fertilized virgin and cultivated Pima clay loam upon repeated extraction with water is a characteristic of the many calcareous soils examined in this investigation. The rather constant pH value of the soil suspensions even after many extractions was some assurance that the hydrogen and hydroxyl conditions in the final suspension were not obviously dissimilar from those of the first. Release of organic phosphorus followed the same trend as that of inorganic phosphorus. Perhaps the same factors influence the release of both forms of phosphates.

TABLE 4

Rate of release of phosphorus from Pima silty clay loam upon repeated extractions with water at a 1:5 ratio

NUMBER OF TIMES EXTRACTED	INORGANIC PHOSPHORUS		TOTAL PHOSPHORUS (IGNITED)		pH OF EXTRACT	
	Wet*	Dried†	Wet	Dried	Wet	Dried
	ppm.	*ppm.*	*ppm.*	*ppm.*		
Virgin soil 16a						
1	7.6	7.6	8.7	8.7		
2	7.5	6.7	7.9	7.3	8.50	8.50
3	6.1	6.0	6.4	6.5	8.50	8.45
4	5.0	4.7	6.0	5.6	8.50	8.50
5	3.0	3.8	3.0	4.2	8.65	8.50
6	2.3	3.2	2.6	3.9	8.60	8.40
7	1.9	2.9	2.8	3.6	8.60	8.40
8	1.7	1.9	2.1	1.8	8.50	8.40
9	1.6	1.4	1.9	1.6	8.50	8.29
10	1.4	1.4	1.8	1.6	8.42	8.25
11	1.0	1.3	1.1	1.5	8.40	8.23
Total	39.1	40.9	44.3	46.3		
Cultivated soil 14						
1	1.90	1.90	2.27		8.65	8.65
2	1.68	1.68	1.82		8.60	8.62
3	1.11	1.20	1.60		8.50	8.54
4	0.92	0.91	1.50		8.50	8.50
5	0.78	0.78	1.20		8.45	8.40
6	0.63	0.73	1.01		8.45	8.40
7	0.36	0.36	0.85		8.30	8.35
8	0.18	0.18	0.75		8.30	8.30
9	0.10	0.10	0.50		8.30	8.25
10	Trace	Trace	0.25		8.30	8.25
11	Trace	Trace	Trace		8.25	8.25
Total	7.66	7.87	11.75			

* Soil kept wet continuously during extraction time.

† Soil air-dried overnight between extractions.

Greenhouse studies

To evaluate the soils more certainly as to their relative phosphate-supplying power, greenhouse studies were made and compared with solubility data of the laboratory. Fifteen soils were selected from those examined in the laboratory, weighed into pots at the rate of 1 kgm. per pot, treated, and seeded to barley and tomatoes. Each of the following treatments was replicated three times for each plant: 100 pounds nitrogen (ammonium nitrate) per acre; 100 pounds nitrogen plus 100 pounds P_2O_5 (superphosphate) per acre; 100 pounds nitrogen plus 250 pounds P_2O_5 (superphosphate) per acre.

Vaughn barley was planted at the rate of 50 seeds per pot and Marglobe tomatoes at 15. After the tomato plants were well started they were thinned to a constant number of 12 per pot. The barley was not thinned. The tops were harvested at the end of 5 weeks and dried at 60° C. to a constant weight. Phosphorus and calcium were determined on the dilute HNO_3 filtrate of the ashed samples.

TABLE 5

Yield, phosphorus, and calcium content of barley tops[*] *grown in the greenhouse on various calcareous soils treated with superphosphate at the rate of 0, 100, and 250 pounds* P_2O_5 *per acre*

SOIL	YIELD			PHOSPHORUS CONTENT			CALCIUM CONTENT			RATIO OF CALCIUM TO PHOSPHORUS		
	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5
	gm.	gm.	gm.	%	%	%	%	%	%			
1a	3.50	4.87	6.04	0.025	0.062	0.078	0.47	0.55	0.50	19	9	6
1b	3.39	3.63	4.44	0.031	0.074	0.090	0.79	0.62	0.60	26	8	7
2	3.69	4.40	5.80	0.027	0.069	0.094	0.51	0.46	0.44	19	7	5
3a	3.34	3.55	4.57	0.031	0.056	0.086	0.68	0.59	0.58	22	11	7
3b	3.45	3.96	4.38	0.026	0.066	0.092	0.73	0.78	0.64	28	12	7
4a	3.80	4.74	4.48	0.040	0.062	0.093	0.57	0.60	0.53	14	10	6
4b	3.87	4.45	4.73	0.019	0.062	0.088	0.69	0.66	0.60	36	11	7
5a	4.16	5.09	5.91	0.038	0.062	0.078	0.45	0.35	0.36	12	6	5
5b	4.17	4.18	4.75	0.025	0.049	0.107	0.52	0.44	0.47	21	9	4
6	4.89	4.62	5.35	0.079	0.149	0.140	0.52	0.64	0.65	7	4	5
7a	3.03	3.74	3.93	0.038	0.079	0.088	0.85	0.56	0.52	22	7	6
7b	3.54	3.28	3.79	0.017	0.089	0.113	0.77	0.78	0.60	45	9	5
11	3.94	4.81	5.63	0.024	0.051	0.081	0.56	0.54	0.53	23	11	7
12	4.14	5.37	5.10	0.027	0.054	0.081	0.36	0.39	0.27	13	7	4
14	4.70	5.01	5.13	0.030	0.065	0.076	0.40	0.50	0.46	13	8	6

[*] Each figure represents an average of two pots, dry-weight basis.

Yield of barley and tomato plants. The weight of the tops of barley and tomato plants grown on the various soils is shown in tables 5 and 6. The yield response of barley to phosphate fertilizer additions was much less than that of tomatoes. Differences in yield between the 0 and the 100-pound treatment for barley were significant only at the 5 per cent level. The differences reached the 1 per cent level at the higher rate of 250 pounds of P_2O_5 per acre. Both phosphorus treatments produced significant differences in yield of tomato tops at the 1 per cent level.

Yield response of both barley and tomatoes on soil 6 to phosphate applications was not significant. According to laboratory tests, this soil was unquestionably well supplied with phosphorus soluble in both CO_2 and water. Soil 14, though less well supplied with soluble phosphorus, had sufficient to be classed as only slightly deficient. Barley grown on this soil responded very little to phosphate treatment, though tomato yields were raised appreciably by both treatments. Yield responses to phosphate for soil 7, which had a moderate amount of soluble phosphorus, were not great. All other soils, according to laboratory solubility tests, were deficient in "available" phosphorus. The greenhouse studies support this finding.

Phosphorus in plants. In all instances, the addition of phosphorus to the soil resulted in a highly significant increase in phosphorus content of the plant (tables 5 and 6). Additions of phosphorus equivalent to 100 pounds of P_2O_5 per acre caused an increase of about twofold in the phosphorus content of barley and tomato plants. Applications of 250 pounds also were acccompanied by distinctly higher amounts of phosphorus in the plants. The percentage of phosphorus in barley tops was very similar to that in tomato tops grown in the same soil. Those soils having the greatest amount of phosphorus soluble in both water and CO_2 solution also had the highest percentage phosphorus in the plant. This was evident for the fertilized as well as the unfertilized plots.

TABLE 6

Yield, phosphorus, and calcium content of tomato tops grown in the greenhouse on various calcareous soils treated with superphosphate at the rate of 0, 100, and 250 pounds P_2O_5 per acre*

SOIL	YIELD			PHOSPHORUS CONTENT			CALCIUM CONTENT			RATIO OF CALCIUM TO PHOSPHORUS		
	0 P_2O_5	100 lb. P_2O_5	250 lb P_2O_5	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5
	gm.	*gm.*	*gm*	%	%	%	%	%	%			
1a	0.54	3.27	3.44	0.007	0.048	0.065	3.95	2.38	2.35	564	50	36
1b	0.22	1.82	3.11	0.009	0.057	0.077	4.50	3.46	2.57	500	61	33
2	1.42	2.92	3.53	0.030	0.059	0.079	3.72	2.69	2.58	124	46	33
3a	0.37	2.61	3.24	0.011	0.041	0.069	4.23	2.58	2.71	384	63	39
3b	0.27	2.83	2.95	0.007	0.039	0.075	4.23	2.53	2.79	604	65	31
4a	0.70	3.13	2.79	0.020	0.055	0.090	4.20	2.83	3.09	210	52	34
4b	0.44	2.55	2.89	0.014	0.049	0.090	4.68	2.70	3.48	334	76	39
5a	1.27	1.55	2.75	0.021	0.084	0.084	2.84	2.87	2.41	133	34	31
5b	0.67	2.08	2.29	0.029	0.053	0.114	3.31	2.88	3.21	114	54	28
6	2.73	2.66	2.88	0.116	0.117	0.091	2.62	2.57	2.93	23	22	32
7a	1.00	2.15	2.40	0.026	0.058	0.098	3.86	2.29	2.86	148	39	29
7b	0.28	1.83	2.65	0.007	0.075	0.131	3.73	3.04	2.98	532	41	22
11	0.68	2.49	3.32	0.018	0.042	0.061	3.68	3.16	2.77	204	75	45
12	0.74	1.85	2.46	0.038	0.072	0.087	3.46	3.36	3.00	91	47	34
14	1.76	2.91	3.30	0.048	0.050	0.079	3.36	2.87	2.80	70	37	39

* Each figure represents an average of 2 pots; dry-weight basis.

Calcium content of plant. The data on calcium content of barley and tomato tops showed that a decrease in percentage calcium of the plant material, as a result of phosphorus applications, was significant at the 5 per cent level for barley receiving 250 pounds of P_2O_5 per acre and at the 1 per cent level for tomato tops receiving both the 100- and 250-pound rate. The lowest calcium content was found in samples taken from soils showing the least yield response to phosphorus. Tomato tops had roughly fivefold more calcium than barley tops. Whether the greater calcium uptake of tomatoes is a factor in the greater demand of tomatoes for "available" phosphorus than of barley cannot be ascertained from this single experiment. The presence of more reserve phosphorus in the barley seed, compared with that of the small tomato seed, must be taken into consideration, however.

Calcium-phosphorus ratios in plants. The ratio of calcium to phosphorus in the barley and tomato tops was calculated to examine more fully the apparent relationship between these two elements and the response to phosphorus fertilization of soils. Data show that the ratios decreased with an increase in phosphorus applied and appeared to reach a rather constant value of about 6 and 24 at the 250-pound rate for barley and tomatoes, respectively. The high values of calcium in tomatoes compared with barley are reflected in the ratios of phosphorus to calcium, which were strikingly higher for the latter. This held true at all levels of phosphate fertilization. The differences in ratios for the different soils tended to be reduced to a minimum with increasing amounts of phosphorus added. Thus differences between the soils that require phosphorus and those that do not are characterized more distinctly by the ratios of the unfertilized soils.

Phosphorus fixation studies

Single extraction. Extraction with CO_2-charged water removed more of the added phosphorus from soils than did water alone (table 7). About 10 to 12 per cent less was removed by the 1:5 water extraction than by the CO_2 extraction. Saturated-paste extracts were even lower in soluble phosphorus. Dried soils released less phosphorus to carbonic acid solution than wet soils. The reverse seemed to occur for soils extracted with water alone.

The soils showing the least available phosphorus had a tendency to retain the most added phosphorus. McClellan loam, soil 4a, for example, retained about 90 per cent of that added at the 100-pound rate and about 83 per cent of that added at the 250-pound rate against water extraction, whereas the good soil, Pima clay loam 14, retained about 76 and 70 per cent for the two levels of phosphorus, respectively.

Multiple extraction. The retention of soluble phosphorus added to soils against repeated extraction of water at a 1:5 ratio for two typical soils is shown graphically in figures 3 and 4. The continual release of phosphorus with repeated extraction is rather surprising. After seven or eight extractions, however, the removal of absorbed phosphorus becomes small. Relative values of these data are more significant than absolute values, since the data used in plotting these figures were obtained by subtracting the amounts of phsophorus found in the extracts of the soils without phosphorous added from those to which 100 and 250 pounds of P_2O_5 were added. The untreated samples were subjected to the same extraction method as those treated with phosphate. Another noteworthy feature of the extractions is that the soil low in available phosphorus, soil 4a, retained more absorbed or fixed phosphorus after 12 extractions than did soil 14, better supplied with native available phosphorus. The amount held by the poor soil 4a, receiving 250 pounds of P_2O_5 per acre, was about 95 pounds after 12 extractions, and that the good soil 14 was 55 pounds. The amounts were less than half this value for the soils treated with 100 pounds of P_2O_5 per acre.

TABLE 7

Phosphorus content of CO_2- and saturated-paste extracts of soils treated with soluble phosphorus at the rate of 0, 100, and 250 pounds of P_2O_5 per acre

SOIL	TREATMENT		PHOSPHORUS CONTENT*		
			CO_2 Extract	1:5 Water Extract	Saturated Paste Extract
			lb.	*lb.*	*lb.*
4a. McClellan loam	None		2.4	0	0
	100 pounds P_2O_5	Wet	14.7	12.9	1.3
		Dried	10.9	10.8	1.4
	250 pounds P_2O_5	Wet	51.0	45.0	3.8
		Dried	46.0	39.1	3.8
7a. McClellan loam	None		9.2	0	0
	100 pounds P_2O_5	Wet	39.1	18.4	1.7
		Dried	36.8	21.1	2.9
	250 pounds P_2O_5	Wet	116.2	71.7	7.9
		Dried	113.1	82.7	13.2
14. Pima clay loam	None		11.1	8.7	0.5
	100 pounds P_2O_5	Wet	37.7	23.3	4.5
		Dried	36.9	25.0	—
	250 pounds P_2O_5	Wet	103.4	76.7	7.8
		Dried	99.6	71.2	—
6. McClellan loam	None		14.7	5.0	1.3
	100 pounds P_2O_5	Wet	48.3	19.9	5.4
	250 pounds P_2O_5	Wet	143.5	80.2	7.8
		Dried	—	82.0	—

* P_2O_5 per acre.

Additional information about the security with which phosphorus added to soils is held against extraction was obtained by putting the extensively water-extracted samples, as described in figures 3 and 4, into water at a ratio of 1:5, bubbling with CO_2 for 15 minutes, and determinine the phosphorus in the clear filtrate. Carbonic acid removed no more phosphorus from these soils than from the same soils not treated with phosphorus (table 8). A certain amount of the added phosphorus was retained in the soil, unextractable or only slowly extractable, according to the data appearing in the last column of table 8.

To approach field conditions more closely, the rate of release of phosphorus added to the same four soils used previously was studied on saturated-paste extracts. A total of 10 extractions were made on soil treated with 100 and 250 pounds of P_2O_5 per acre. The soils were allowed to become nearly dry after each extraction. Data in table 9 show that the amount of phosphorus in the tenth paste extract was not always less than that in the first. Furthermore, the greatest amount of phosphorus in solution appeared not always in the first extract but most frequently in the third. Pima clay loam soil 14 appears to be an exception. The higher concentration of salts in the saturated-paste extracts as compared with more dilute extracts may be responsible for phosphate suppression in the first extracts.

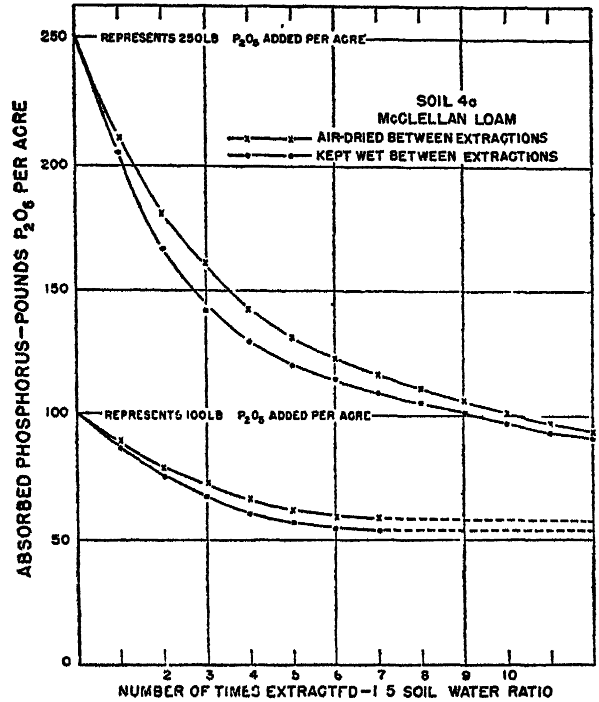

FIG. 3. RELEASE OF PHOSPHORUS ADDED TO MCCLELLAN LOAM AS A RESULT OF SUCCESSIVE EXTRACTIONS WITH WATER AT A RATIO OF 1:5 AS INFLUENCED BY WETTING AND DRYING.

Biological fixation. Six soils were selected and incubated with glucose and nitrate at a C/N ratio of about 12:1 and a concentration of 0.25 per cent carbon to demonstrate that, if phosphorus fixation is to be shown, a source of carbon must be available to provide energy for microbial activity during incubation. Soil in 100-gm. samples was supplied with the glucose-nitrate solution and incubated under optimum moisture conditions at room temperature for 7 days. A second set of soils was incubated under similar conditions but without additions of glucose or nitrate. A third set was treated with glucose and nitrate but spread to dry immediately. Drying was accomplished in a few hours. After

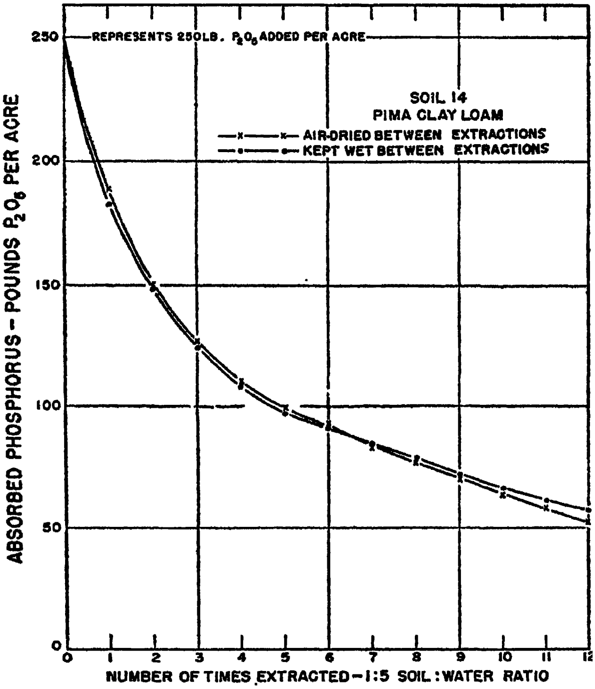

FIG. 4. RELEASE OF PHOSPHORUS ADDED TO VIRGIN PIMA CLAY LOAM, RICH IN AVAILABLE PHOSPHORUS, AS A RESULT OF SUCCESSIVE EXTRACTIONS WITH WATER AT A RATIO OF 1:5 AND AS INFLUENCED BY WETTING AND DRYING.

TABLE 8

Susceptibility of phosphorus absorbed by four soils to extraction with carbonic acid solution

SOIL	INITIAL TREATMENT, P_2O_5 PER ACRE	TIMES EXTRACTED WITH WATER AT 1:5 RATIO	CO_2-SOLUBLE PHOSPHORUS		PHOSPHORUS FIXED OR UNEXTRACTABLE
			Before treatment	After treatment and extractions	
	lb.		*ppm.*	*ppm.*	*ppm.*
4a. McClellan loam	100 Wet	7	0.38	0.67	9.0
	100 Dried	7	0.38	0.69	9.9
	250 Wet	12	0.38	0.80	20.4
	250 Dried	12	0.38	0.71	19.8
7a. McClellan loam	100 Wet	9	2.00	1.99	6.8
	100 Dried	8	2.00	1.81	6.8
	250 Wet	12	2.00	2.00	17.0
	250 Dried	12	2.00	2.24	10.0
14. Pima clay loam	100 Wet	6	2.12	1.80	5.3
	100 Dried	6	2.12	1.82	5.0
	250 Wet	12	2.12	2.00	12.5
	250 Dried	13	2.12	1.86	9.9
6. McClellan loam	100 Wet	11	3.21	1.21	4.0
	250 Dried	12	3.21	1.27	10.6

incubation or drying, the soils were extracted with 1:5 water and again supplied with glucose and nitrate as required. Only data on total water-soluble phosphorus are presented for the three soils low in phosphorus, 1a, 4a, and 7a, whereas water-soluble inorganic phosphorus figures are given for the soils adequately supplied with phosphorus, 6, 14, and 16a. Data in table 10 show that the greatest amount of phosphorus extracted from phosphorus-poor soils came from those incubated with glucose and nitrate. The influence of incubation without glucose and nitrogen treatment was negligible. The increase in water-soluble organic phosphorus of these soils is due to the demand of the microorganisms for phosphorus, which resulted in release of insoluble mineral phosphorus and conversion

TABLE 9

Influence of repeated extraction on concentration of phosphorus found in saturated-paste extract of four soils treated with soluble phosphate at the rate of 0, 100, 250 pounds per acre

Gamma P extracted per 100 gm. soil

NUMBER OF EXTRACTIONS	P EXTRACTED			P EXTRACTED		
	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5	0 P_2O_5	100 lb. P_2O_5	250 lb. P_2O_5
	4a McClellan loam (cultivated)			*6 McClellan loam (cultivated)-ignited*		
1	0	28	164	14	27	84
2	0	33	157	14	30	86
3	0	46	180	14	25	100
4	0	43	150	14	30	119
5	0	39	163	9	29	116
6	0	43	150	9	33	91
7	0	35	123	8	30	87
8	0	26	71	8	25	85
9	0	24	71	8	24	81
10	0	24	70	7	31	97
Total ..		341	1309	103	284	946
	14 Pima clay loam (cultivated)			*16a Pima silty clay loam (virgin)*		
1	12	99	171	16	61	175
2	13	61	167	16	85	226
3	12	75	167	35	221	367
4	10	40	150	27	173	350
5	9	52	93	26	105	325
6	9	52	109	23	112	250
7	9	45	109	26	78	229
8	9	62	98	21	73	186
9	10	57	104	28	105	178
10	8	56	103	28	105	178
Total	101	509	1271	246	1118	2464

to the organic form. The decrease in the water-soluble inorganic phosphorus of the three phosphorus-high soils was caused by conversion of the inorganic phosphorus to the organic form. Thus incubation with glucose and nitrate caused a marked decrease in water-soluble inorganic phosphorus.

The fixation of phosphorus in soil solutions by soil microorganisms may be readily demonstrated by extracting soils with water, adding a carbon source and incubating the resulting solution. Soil solutions were prepared by shaking 200 gm. of soil with 500 ml. of distilled water in an end-over-end shaker for 1 hour and filtering in a Büchner funnel with vacuum. One hundred ml.-portions of the clear filtrate were placed in a 500-ml. flask in duplicate and treated as follows: 1. No treatment; 2. 20 gamma of P; 3. Glucose plus nitrate (12:1, rate of 0.25 per cent carbon); 4. 20 gamma of P plus glucose and nitrate as above.

TABLE 10

Influence of incubating six soils with additions of glucose and nitrate on quantity of phosphorus extracted by water at a ratio of 1:5

Phosphorus expressed in ppm. soil

EXTRACTION	WATER-SOLUBLE ORGANIC PHOSPHORUS								
	Soil 1a Mohave sandy loam			Soil 4a McClellan loam			Soil 7a McClellan loam		
	1*	2†	3‡	1	2	3	1	2	3
1	1.00	1.00	1.09	0.72	0.72	0.79	1.13	1.13	1.20
2	0.50	0.50	0.88	0.52	0.50	0.60	0.40	0.40	0.45
3	0.32	0.30	0.59	Trace	Trace	0.33	Trace	Trace	0.45
4	Trace	Trace	0.35	Trace	Trace	Trace	Trace	Trace	0.33
Total....	1.82	1.80	2.91	1.24	1.22	1.73	1.53	1.53	2.43
	WATER-SOLUBLE INORGANIC PHOSPHORUS								
	Soil 6 McClellan loam			Soil 14 Pima clay loam			Soil 16a Pima clay loam		
	1	2	3	1	2	3	1	2	3
1	4.31	4.31	4.14	3.57	3.50	2.36	7.60	7.60	7.00
2	3.28	3.50	1.57	2.96	2.95	2.20	6.70	6.60	5.29
3	2.07	2.10	1.57	2.13	2.20	1.33	6.00	6.15	4.93
4	1.81	1.73	Trace	1.50	1.70	1.21	4.70	4.80	2.97
Total.....	11.47	11.44	7.28	10.16	10.35	7.10	25.00	25.15	21.19

* 1 = no glucose or nitrate; incubated.

† 2 = glucose and nitrate; spread to dry.

‡ 3 = glucose and nitrate; incubated.

The solutions were allowed to incubate 180 days at 30° C. Aliquots for phosphorus were taken after 0, 2, 3, 4, 14, 30, and 180 days of incubation.

The influence of carbon and nitrogen on the quantity of inorganic phosphorus found in the 1:2.5 water extracts from four soils is shown in table 11. The presence of an available carbon source such as glucose caused an immediate immobilization of inorganic phosphorus in all soil solutions. In absence of an available energy source, fixation by microorganisms is negligible; in fact, liberation of phosphorus from the organic form is indicated. McClellan loam, 4a, and Mohave sandy loam, 1a, released no phosphorus to water extraction, whereas Cajon sandy loam, 15, and Pima clay loam, 16a, yielded fair amounts of water-soluble inorganic phosphorus. Figure 5 shows that, 7 days after incubation, microbial growth was much greater in solutions supplied with glucose. According to the turbidity, which indicates the presence or activity of microorganisms, phosphorus alone permitted only slightly more growth than solutions without treatment. This circumstance varies with the amount of organic matter in the extract. Only after 6 months of incubation did phosphorus begin to mineralize

TABLE 11

Influence of added carbon and nitrogen on quantity of inorganic phosphorus found in soil extracts (1:2.5) incubated over a period of 6 months

Phosphorus expressed in ppm.

TREATMENT	TIME OF INCUBATION						
	0	2 days	3 days	4 days	14 days	30 days	180 days
				Pima clay loam 16a			
None	3.18	3.34	3.18	3.30	3.45	3.55	4.38
P*	5.50	5.72	5.72	5.72	5.98	6.50	6.50
N+C†	3.18	0	0	0	0	0	Trace
P+N+C	5.50	Trace	0	0	0	0	0.1
				McClellan loam 4a			
None	0	0	0	0	0	0	Trace
P	2.95	2.66	2.82	2.75	2.75	—	2.95*
N+C	0	0	0	0	0	0	Trace
P+N+C	3.30	0	0	0	0	0	Trace
				Mohave sandy loam 1a			
None	0	0	0	0	0	0	Trace
P	3.30	3.30	2.70	3.30	3.30	3.50	3.55
N+C	0	0	0	0	0	0	0
P+N+C	3.30	0	0	0	0	0	Trace
				Cajon sandy loam-silted phase 15			
None	1.88	1.62		1.72	1.88	2.22	3.46
P	1.00	1.02	1.02	1.02	4.20	4.55	4.75
N+C	1.88	0	0	0	0	0	0.76
P+N+C	1.10	0	0	0	0	0	1.07

* P = 20 gamma of phosphorus added to the P and P+N+C treatments per 100 ml of extract

† N+C = carbon and nitrogen added in a ratio of 12.5:1 at the rate of 0.25 per cent carbon.

The rather slow liberation of inorganic phosphorus from microbially bound form was rather surprising. The data emphasize the dependency of soluble inorganic soil phosphorus on the carbon cycle of the soil.

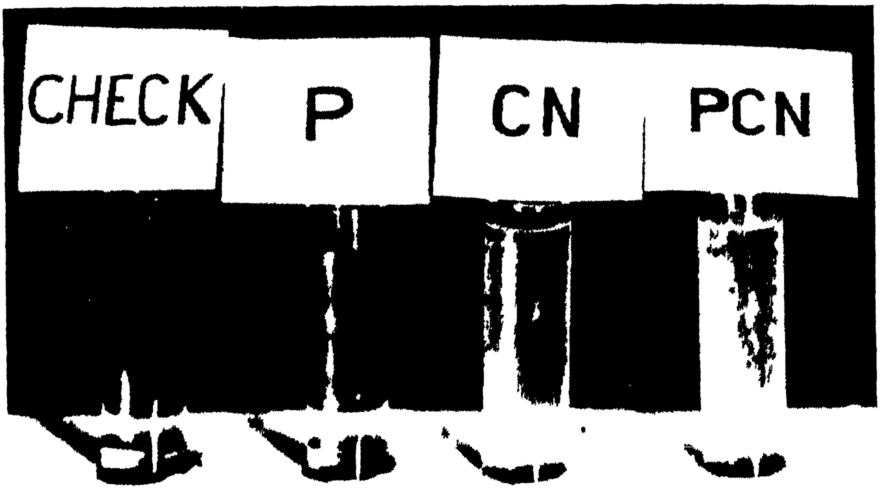

Fig. 5. Influence of Carbon and Nitrogen on Microbial Activity and Phosphorus Fixation in Soil Extracts

DISCUSSION

Detailed greenhouse studies show that availability of soil phosphorus to plants in closely related to the amount of soluble phsophorus found in extracts of water and carbonic acid. The importance of water in the role of phosphorus availability in soils is emphasized by the finding that additional phosphorus is released upon repeated extraction with water and that the greater the dilution of soil with water, the greater the solubility of phosphorus. The rather uniform decrease, to a minimum, in quantity of soluble phosphorus removed with successive extractions of water indicates that this small portion is wholly different from the larger water-insoluble portion of phosphorus. That wetting and drying in these highly calcareous soils had but little influence on the rate or amount of water-soluble phosphorus extracted also supports this belief. The gradual decline in amount released with each extraction also may be interpreted to mean that a single mechanism is involved in release of water-soluble phosphorus. This has additional support in the fact that a portion of the organic phosphorus follows the same extraction characteristic as the inorganic.

The data presented in this study show that there was little correlation between carbonate calcium and soluble phosphates in different surface soils. It may be assumed that the quantity of calcium in these soils is so great that quantitative analyses are of no value but that the "activity" of the calcium as controlled by its physical and chemical form is of prime importance. The attempt to determine "active" calcium by use of ammonium oxalate solution was not wholly successful. An extensive study of the calcium-phosphorus relationships of soil extracts is now underway and promises to prove enlightening.

Not all the phosphorus added to calcareous Arizona soils is readily fixed in a wholly insoluble form. Single extractions with water or CO_2-water would lead one to believe that a rather large amount of phosphorus added to calcareous soils is fixed or absorbed by the soil. Data obtained by extracting the soil with successive portions of water show, however, that only a small amount of added soluble phosphorus is fixed in an insoluble form. Only this small amount appears to have the characteristic of carbonato-apatite. The finding that added phosphorus is released in considerable quantities even after many extractions and that a large amount is recovered in this manner supports the field observations that the effects of phosphorus fertilizers added to irrigated Arizona soils may influence crop production for many years after application.

Fixation of phosphorus by microorganisms in an organic form was clearly shown to depend upon the presence of an available source of carbon. The extent of microbial fixation in soils undoubtedly varies considerably between different soils and with the same soil at different times of the year. Variation in the available carbon may be partly responsible for the variations in available phosphorus often observed within the same field at different sampling periods. Retardation of growth in crops planted immediately after plowing under of large amounts of plant materials may be caused by microbiological fixation of phosphorus as well as nitrogen. Immobilization of available phosphorus by this means would be expected to be most serious in soils that are intensively farmed and in soil after plowing down of plant residues low in phosphorus. Such a circumstance is common to many irrigated soils in Arizona. Many farms raise two and three crops a year with no rest period to allow decomposition of plant residues.

SUMMARY

The water and carbonic-acid solubility of native phosphorus of 20 calcareous Arizona soils was studied. The availability of the soil phosphorus to barley and tomatoes was compared to the solubility determinations made in the laboratory. There was a distinct relationship between the amount of water and carbonic-acid-soluble phosphorus and availability of the phosphorus of the soil to plants.

High carbonate calcium and "active" calcium were correlated with low amounts of water and carbonic-acid-soluble phosphorus only at different depths within a single soil. This relationship did not hold for different surface soils.

The water-soluble phosphorus of soils was not removed completely by one extraction but continued to appear in diminishing amounts in successive extracts. The ratio of water to soil influenced the amount of soluble phosphorus in the extracts.

The extent of fixation or absorption of phosphorus added to some calcareous soils was investigated. Results indicate that only a small portion was securely fixed against extraction with water. Fixation by microorganisms depends upon the amount of available carbon present in the soil and the activity of the microorganisms under certain farming circumstances. In soils low in "available" phosphorus, this form of fixation is indicated to be serious in limiting crop production.

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THE HYPOIODITE METHOD FOR STUDYING THE NATURE OF SOIL ORGANIC MATTER: I. PRINCIPLES, PRETREATMENT, AND CONDITIONS AFFECTING THE EXTENT OF REACTION[1]

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Received for publication September 12, 1949

Apart from the very general trends discernible in the data for proximate analysis and C/N ratios, little success has been achieved in the specific correlation of the chemical nature of soil organic matter with soil type or even groups (1, 28, 30), although there is evidence that soil organic matter does differ significantly in chemical nature from one soil type to another (7, 21, 29).

The failure of quantitative methods based on solubility characteristics (proximate analysis) or total elemental content (C/N relationships) to detect real differences in the nature of soil organic matter points to the necessity for distinguishing differences in quality as well as in quantity. One method that offers distinct possibilities of advancing our knowledge of soil organic matter is the hypoiodite method proposed by Norman and Peevy (16), in which a semispecific reagent for groups characteristic of lignin is employed. This method was modified by Norman (17). NaOI is a mild oxidizing agent that reacts with phenolic nuclei through the phenolic hydroxyl, with aldehydes, and to a limited extent with other groupings.

This paper is chiefly concerned with a review of the principles and reactions involved in hypoiodite oxidation, a critical evaluation of pretreatment, and results of a critical study of conditions affecting the extent of hypoiodite oxidation.

REACTIONS OF HYPOIODITE

Although considerable information is available on hypohalites in general, there are relatively few data on hypoiodite. The active reagent, NaOI, exists only in alkaline solution, and then only briefly, in contrast with the more stable NaOCl and NaOBr, which exist in acid as well as in alkaline solution. In this very instability lies the special value of NaOI as a tool in organic matter research. When I_2 and NaOH are mixed in the presence of organic matter

$$I_2 + 2NaOH = NaOI + NaI + H_2O \qquad (1)$$

the NaOI formed enters into two competitive reactions which proceed simultaneously: reaction with organic matter

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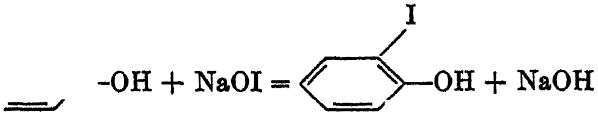
[1] Published as Scientific Paper No. 864, Agricultural Experiment Stations, Institute of Agricultural Sciences, State College of Washington, Pullman. Taken from a thesis submitted to the faculty of the State College of Washington in partial fulfillment of the requirements for the degree of doctor of philosophy. The writer wishes to express his appreciation to S. C. Vandecaveye and H. W. Smith for the many helpful suggestions and criticisms tendered during the course of this study and the preparation of the manuscript.



(*2*)

and with itself

$$3NaOI = NaIO_3 + 2NaI \qquad (3)$$

As a result there is an abrupt ending to the reaction when the excess NaOI is converted to $NaIO_3$ and NaI, which have a negligible oxidizing action at room temperature. The oxidation of organic matter is not complete and is limited to readily oxidizable groupings because of the rapidity with which the reaction represented by equation (*3*) proceeds. Upon completion of the oxidation, the excess iodine, then in the form of $NaIO_3$ and NaI, can be converted to I_2, and subsequently determined by titration with thiosulfate. Thus the measure of I_2 consumed by the organic matter[2] is the difference between the I_2 added and that recovered.

A survey of the reactions of NaOI with organic compounds reveals three principal courses by which I_2 may be consumed: (*a*) in the oxidation of aldehydes, (*b*) in the iodoform reaction, and (*c*) in substitution in phenolic compounds. It seems probable that the reaction of NaOI with phenolic compounds will account for the major part of the I_2 consumed, since this reaction is rapid, the iodoform reaction is relatively slow, and aldehydes are probably not present naturally in appreciable quantity (16).

Sodium hypoiodite has been used widely as a general reagent for aldehydic groups in various carbohydrates (5, pp. 895–901; 13; 19; 20). Although aldehydic groups are not thought to occur naturally in soil organic matter, their formation under the conditions of hypoiodite oxidation is not to be ruled out, since cleavage and other conversions of carbohydrates in alkaline solution lead to overoxidation and some formation of iodoform (18). The consumption of I_2 by carbohydrates will vary according to the conditions of oxidation.

The iodoform reaction requires the presence of the aceto-group, $CH_3\text{-}C{=}O$, joined to a H atom or a C atom which does not carry highly activated H atoms or groups capable of high steric hindrance (6). Any group capable of yielding the aceto-group will also give an iodoform reaction. The odor of iodoform is apparent from all NaOI-treated soils examined by the author.

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[2] Throughout this and the following paper, as well as those of Norman and his co-workers, the quantity of I_2 reported is that amount measured by titration with thiosulfate, and not the amount consumed by the organic matter. The quantity of I_2 actually consumed by the organic matter is half that found by titration with thiosulfate. This is because one mole of NaI is formed for each mole of NaOI (*1*) but only the NaOI is involved in the raction with organic matter. Upon acidification, only that amount of NaI is recovered which is equivalent to the excess of NaOI: for each mole of NaOI used in reaction with organic matter, a mole of NaI is effectively placed beyond recovery. Although this fact is essential to a full understanding of the chemistry of hypoiodite reactions, practically it may be ignored, since the values obtained are used only in the relative sense.

The substitution of I_2 in phenols may be represented by equation (*2*). The phenolic hydroxyl is the point of attack, the substitution being in the ortho and para positions. Polyhydric phenols may be oxidized as well as iodinated. The consumption of I_2 by phenolic compounds may proceed along one or both of two paths: substitution primarily in free ortho and para positions, with or without subsequent oxidation. The rate of substitution will be very rapid and the rate of oxidation comparatively slow (32). The amount of I_2 consumed, therefore, will depend upon the presence of the free hydroxyl group, the molecular configuration which will determine the number of free ortho and para positions, and the susceptibility of the whole molecule to oxidation.

Although NaOI is a mild oxidizing agent, the total reaction with organic matter cannot be considered one of oxidation. The iodoform reaction and the reaction with phenolic compounds are dominantly substitution reactions. Thus the main reaction appears to be with the phenolic substances of the soil, which in effect means with the lignin in the soil. Since the agencies and processes of decomposition should vary in nature and intensity with variations in soil-forming conditions, the residual organic matter should also vary in composition and condition. If these changes involve the lignin molecule and more specifically its phenolic nature, the use of NaOI should reflect the changes at least to the extent that reactive groupings are unaffected by combination with other organic or inorganic constituents of the soil.

The level of use of I_2 depends primarily upon the amount and nature of organic matter, since the reaction is confined to certain groupings. Since no means are available for quantitative determination of these groups, the amount of I_2 consumed per unit of carbon in the soil is the only means of expression that has analytical significance. The most suitable means of expression is in milliequivalents of I_2 consumed per gram of carbon, which for convenience may be termed the "activity index."

AN EXAMINATION OF PRETREATMENT

Norman (17) has demonstrated that pretreatment with HCl-KI solution increases the consumption of I_2. According to him:

> Many soil samples have been found to have a component which causes the release of iodine from iodide. Unless the amount so released be separately determined or release prevented, this causes the amount of iodine apparently used in the hypoiodite oxidation to be lower than actual. Two or three samples have been found on which the iodine so released is in excess of the iodine utilized . . . This disturbing factor is usually larger and proportionately far more serious in its effects in subsurface soils than in surface samples . . .Preliminary studies of the nature of the disturbing material, which has virtually the properties of a peroxide, indicate that it is predominantly, but not exclusively, inorganic. The inorganic components may be biologically oxidized manganese and iron.

Because the action of pretreatment was not clear and explanations other than that suggested by Norman (17) may be offered for at least part of the increase in I_2 consumption due to pretreatment, the whole process of pretreatment has been examined critically.

Methods and materials

The procedure of Norman (17) was used throughout. Except for the introduction of pretreatment and the substitution of 10 ml. of 3 *N* NaOH for 25 ml. of *N* NaOH, this procedure does not differ significantly from the original procedure proposed by Norman and Peevy (16).

The effect of various oxidants and reductants was investigated in synthetic systems. In these cases reagent quality salts were used. The soils used to study the effects of pretreatment were selected to represent a wide range in chemical characteristics.

Effect of inorganic oxidants

Oxidants normally expected in soil systems are limited to Fe^{+++} and the higher oxidation states of Mn that are easily capable of solution. The reactions presented by equations (*4*) and (*5*) would go substantially to completion, as is indicated by the equilibrium constants:

TABLE 1

Effect of manganese dioxide upon blank values

TREATMENT	0.03 *N* THIOSULPHATE USED PER 10 ML. ALIQUOT	
	First end point	Second end point*
	ml.	*ml.*
Blank	17.08	0
Blank + 0.2 per cent MnO_2		
Supernatant liquid	17.04	0
Suspension of		
Low density	17.25	0.35
Medium density	17.34	0.60
High density	17.84	1.0

* I_2 formed on standing for 3 minutes after the first end point.

$$Fe^{+++} + I^- = Fe^{++} + \tfrac{1}{2} I_2 \qquad K_c = 4 \times 10^3 \qquad (4)$$

$$MnO_2 + 4H^+ + 2I^- = Mn^{++} + I_2 + 2H_2O \qquad K_c = 1 \times 10^{17} \text{ (pH 2.0)} \qquad (5)$$

In an alkaline medium, however, the concentration of Fe^{+++} is negligible, limited by the solubility product of 1.1×10^{-36} (8, p. 1251). Similarly, Mn in the higher oxidation forms, probably as pyrolusite (23) is considered generally to be insoluble and not reducible by I^- in alkaline medium (11, pp. 345, 350).

In synthetic systems, the addition of Fe^{+++}, Mn^{+++}, or MnO_2 did not increase the titration values of blanks (14), indicating that these oxidants do not oxidize I^- to I_2 in alkaline medium. The data in table 1 concerning the comparison of the blank and supernatant liquid of MnO_2-treated blanks are typical for these three oxidants. It was noted, however, that suspensions of MnO_2 did oxidize I^- to I_2 to a small extent in neutral solutions and rapidly and extensively in acid solutions (14). This observation points to a source of error contributed by inorganic oxidants when suspensions are acidified and titrated. The data in table 1 illustrate the possible error contributed by titrating suspensions. Aliquots of the supernatant liquid and of various suspensions of MnO_2 (ground pyrolusite) were taken from blanks made up to contain 0.2 gm. of MnO_2 per 100 ml., acidified with 10 per cent HCl, and immediately titrated with thiosulfate. Any I_2 formed within 3 minutes following this end point was also titrated. Obviously, MnO_2 does not oxidize I^- to I_2 in alkaline suspension and any error introduced occurs during the titration phase of the procedure. If suspended matter is allowed to settle out before aliquots are taken for titration, no serious interference from MnO_2 occurs unless it has been peptized to colloidal dimensions by the NaOH. Although not indicated in these data, the rate of solution of MnO_2 is slower in H_3PO_4 than in HCl suspension. The use of supernatant liquid greatly simplifies recognition of the end point.

Effect of inorganic reductants

An examination of the possible reactions of Fe and Mn with KI in HCl solution suggests another explanation that may account, at least in part, for the observation of Norman (17) that the consumption of I_2 by soils is increased by pretreatment. This greater usage of I_2 may be attributed to the *introduction of reductants* that reduce the added I_2 rather than to the elimination of an oxidant which oxidizes I^- to I_2.

It has been shown that Fe^{+++} is reduced in the cold to Fe^{++} in the presence of acids, certain salts, and organic substances (15, 27), provided the pH is less than 5.0 and the Fe is in cationic form (3). At pH values characteristic of pretreatment (approximately 2.0) there is an appreciable solution of Fe and a substantial reduction of Fe^{+++} to Fe^{++} by I^- (*4*), which has a higher reduction potential than organic matter. Sherman and Harmer (23) and others (12, 24, 25, 26) have concluded that the condition of Mn in the soil is best represented by the equilibrium,

soluble $Mn^{++} \rightleftarrows$ *replaceable* $Mn^{++} \rightleftarrows$ *easily reducible* $MnO_2 \rightleftarrows$ *inert* MnO_2,

which is displaced to the right in alkaline soils and to the left in acid soils to an extent variable with the oxidation-reduction potential of the soil. The equilibrium constant calculated from normal electrode potentials for the reaction, $MnO_2 + 4H^+ + 2I^- = Mn^{++} + I_2 + 2H_2O$, is approximately 1×10^{17} at pH 2.0 but unity or less in the pH range 6 to 7. Thus, an extensive solution and reduction of MnO_2 to Mn^{++} by the HCl-KI solution used during pretreatment may be expected.

The seriousness of introducing Fe^{++} and Mn^{++} into the system depends upon the fact that their hydroxides, unlike $Fe(OH)_3$ and MnO_2, are appreciably soluble in alkaline medium and are readily oxidized therein (2, p. 122; 4; 22, p. 2079).

It has been shown by experiment (14) that the inorganic reductants Fe^{++} and Mn^{++} have an appreciable influence upon the I_2 consumption. In alkaline medium the freshly precipitated hydrous oxides of Fe^{++} and Mn^{++} are sufficiently soluble to be oxidized by I_2 or NaOI. When the standard pretreatment with

HCl-KI and hypoiodite oxidation (17) was applied to blanks containing $FeCl_3$ there was an extensive formation of Fe^{++} and I_2 was consumed (14). In the presence of organic matter this utilization of I_2 by the Fe^{++} formed by pretreatment would have the effect of increasing the activity index for the organic matter. Although the reaction, $Fe^{+++} + I^- = Fe^{++} + 1/2\ I_2$, under the proper conditions goes substantially to completion, addition of sufficient F^-, H_3PO_4, or $H_4P_2O_7$ to form little-ionized complexes with Fe^{+++} may so reduce the concentration of the Fe^{+++} ion that no I_2 is liberated from a mixture containing I^- (9, p. 484). Application of this principle with a view toward preventing the formation of Fe^{++} was only partly successful. In synthetic mixtures, H_3PO_4 was found substantially to reduce, but not to inhibit, the oxidation of I^- to I_2 and to have absolutely no effect upon the reduction of I_2 by Fe^{++} in alkaline medium (14).

The amounts of Fe^{++} formed from Fe^{+++} in the presence of I^- and H_3PO_4 were sufficiently small that a qualitative study of the comparative solvent action of HCl and H_3PO_4 with and without KI (at pretreatment concentrations) upon the Fe and Mn of eight soils was undertaken. Soil-water and soil-acid suspensions were shaken for 4 hours, treated with a small amount of saturated alum, and filtered after an additional 30 seconds of shaking. Qualitative tests for Fe^{+++}, Fe^{++}, and Mn^{++} ions and quantitative measurement of the free I_2 were made on portions of the filtrate. Representative data from four of the eight soils are presented in table 2 (14). It is implicit in these data that pretreatment with HCl-KI does produce significant quantities of Fe^{++}, and that the reduction of Fe^{+++} to Fe^{++} is accomplished by I^-. HCl extracted appreciably more Fe^{+++} from all soils than did the H_3PO_4. Only traces of Fe^{++} were found in the HCl, H_3PO_4, or H_3PO_4-KI extracts, whereas strongly positive tests were obtained on the HCl-KI extracts. Although water-soluble Mn^{++} was found in some soils, acid extractions were markedly more efficient. Little difference was noted in the ability of the two acids to extract Mn^{++}, and, contrary to expectation, KI had little effect in increasing the extraction. These data show conclusively that the formation of reducing ions of one form or another may be anticipated when soils are pretreated with acids or acid solutions of KI.

Pretreatment and oxidation were then applied to Palouse silt loam, comparable strengths of HCl and H_3PO_4 being used at two concentrations and compared with no pretreatment. The data are summarized in table 3. Consistent with expectation, pretreatment with HCl-KI solution did increase the consumption of I_2 and to an extent in proportion to the strength of the acid. The actual reduction in I_2 consumption due to pretreatment with H_3PO_4-KI was wholly unexpected. No explanation is offered for this result. These results point strongly to the conclusion that the solution of Fe^{+++} and its reduction to Fe^{++} during pretreatment is a contributing factor in increasing the amount of I_2 used by soils.

Discussion

The data presented show that pretreatment with HCl-KI solution increases the amount of I_2 consumed by soil over the amount consumed by soil not so treated and that it also dissolves appreciable quantities of Mn^{++} and of Fe^{+}

TABLE 2

Solvent action of HCl and H_3PO_4, with and without KI, upon the Fe and Mn in different soils

SOIL	TREATMENT	PRESENCE OF IONS ON QUALITATIVE TEST*			I_2 FORMED PER 100 GM. OF SOIL
		Fe^{+++}	Fe^{++}	Mn^{++}	
					me.
Olympic clay loam	Water	−	−	+	—
	HCl	+++	±	+++	—
	HCl-KI	++	+++	+++	0.89
	H_3PO_4	++	−	+++	—
	H_3PO_4-KI	++	±	+++	0.38
Palouse silt loam	Water	−	−	+	—
	HCl	++++	+	+++	—
	HCl-KI	++	++++	+++	1.44
	H_3PO_4	+++	±	+++	—
	H_3PO_4-KI	++	±	+++	0.24
Hesson clay loam	Water	−	−	++	—
	HCl	+++	±	++++	—
	HCl-KI	+++	+++	+++++	1.25
	H_3PO_4	++	±	+++++	—
	H_3PO_4-KI	++	±	+++++	0.48
Sagemoor fine sandy loam	Water	−	−	−	—
	HCl	+++	±	+++	—
	HCl-KI	++	+++	+++	2.16
	H_3PO_4	++	±	+++	—
	H_3PO_4-KI	+	±	+++	0.28

* A plus indicates a positive test, a minus a negative test. The combination of plus and minus indicates a doubtful test, which probably is best considered as negative.

TABLE 3

Effect of pretreatment with HCl-KI and H_3PO_4-KI solutions upon the pH and I_2 consumption of Palouse silt loam

TREATMENT	SAMPLE	pH	I_2 PER GRAM OF CARBON, AVE.
			me.
Pretreatment			
10% HCl + KI	Blank	0.90	
	Soil	1.20	5.76
20% HCl + 1% KI	Blank	0.70	
	Soil	0.70	6.48
4% H_3PO_4 + 1% KI	Blank	1.3	
	Soil	2.3	4.26
8% H_3PO_4 + 1% KI	Blank	0.90	
	Soil	1.90	3.89
No pretreatment			
Water	Blank	6.7	
	Soil	6.7	4.37

much of which is reduced to Fe^{++}. Since the Fe^{++} and Mn^{++} so formed can reduce I_2 in alkaline solution, they may to a considerable extent be responsible for the increased consumption of I_2 due to pretreatment. In proposing pretreatment with HCl-KI solution as a means for removing disturbing oxidants which oxidize I^- to I_2, Norman (17) apparently overlooked this aspect of pretreatment. Pretreatment will remove oxidants which oxidize I^- to I_2 but it will also introduce reductants which will reduce I_2 to I^-. Thus the benefit obtained by destroying disturbing oxidants could be offset by the error contributed by the introduction of reductants. As it is difficult to conceive of a soil that will not provide some Fe^{++} to a solution 10 per cent in HCl and 1 per cent in KI over a period of 12 to 15 hours, the use of this particular pretreatment solution should be abandoned.

No explanation is offered for Norman's observation (17) that in some cases the I_2 released from I^- by oxidants exceeds the I_2 utilized. Such negative results have not been observed by this investigator. Although it is probable that some portion of the increased I_2 consumption resulting from pretreatment as observed by Norman is due to the formation of reductants during pretreatment rather than to elimination of oxidants, it is not suggested that this reaction of pretreatment is wholly responsible for the observed increases. It has been shown, however, that the common inorganic oxidants of soils, Fe^{+++} or MnO_2, should not be responsible for the oxidation of I^- to I_2 *in alkaline medium.* In this study, organic oxidants and peroxides have not been considered, and their presence or absence is not debated. These types of compounds may be responsible for Norman's negative results. The observation reported here that pretreatment with H_3PO_4-KI solution does not increase I_2 consumption and minimizes the formation of Fe^{++} may be of some value to an investigation of the problem encountered by Norman. Considerable investigation of this reagent will be necessary before it can be accepted for use, inasmuch as H_3PO_4 does not prevent the formation of Mn^{++} and in the one instance reported it has resulted in a reduced I_2 consumption.

CONDITIONS AFFECTING THE EXTENT OF HYPOIODITE OXIDATION

Norman and Peevy (16) have demonstrated that the extent of oxidation of organic matter by hypoiodite is incomplete and is dependent upon the ratio of hypoiodite to organic matter. A systematic examination of the effect upon the extent of oxidation of such variables as I_2, I^-, and NaOH concentrations, as well as size and fineness of sample, was undertaken with a view toward a better understanding of the hypoiodite method and selection of optimum conditions for efficiency and reproducibility.

Methods and materials

The basic procedure used was that of Norman and Peevy (16) modified to the extent that the supernatant liquid was sampled for titration and acidified with 6 N H_3PO_4. Each sample of soil or other material and each parallel blank were treated with 25 ml. of water, 25 ml. of NaOH, and 50 ml. of 0.1 N I_2 in succession, set aside in the dark, and shaken at 10-minute intervals. At the end of 1 hour, 10-ml. aliquots were pipetted into 75 ml. of water, acidified with 5 ml. of 6 *N* H_3PO_4, and titrated with 0.03 *N* $Na_2S_2O_3$. The results, expressed in terms of milliequivalents of I_2 used per 100 gm. of soil or per gram of carbon, are reported on the moisture-free basis and, in the case of lignin, also on an ash-free basis.

The soils used will be described in part II of this series. Soil material from the A horizon passing a 16-mesh sieve was employed unless otherwise specified. A sample of commercial lignin, Meadol,[3] was used as a comparison with soil organic matter. A typical analysis for such material is reported by Wallerstein, Alba, and Hale (31).

Effect of varying concentration of the basic hypoiodite reagents

Changes in efficiency of oxidation as a result of varying concentration of I_2, I^-, and NaOH are probably due to varying stability of the OI^- ion. In an extensive investigation Li and White (10) concluded that the stability of the OI^- ion is dependent upon the I^--and OH^--ion concentrations and that the specific reaction rate of decomposition of OI^- is a linear function of the I^-/OH^- ratio.[4]

Data are presented in figure 1 and table 4 to illustrate the effect of varying concentrations of OH^- and I^- upon the consumption of I_2 by lignin and two soils. Samples providing 52 mgm. of carbon for the soils and 32.4 mgm. of carbon for the lignin were employed. As is predictable from the data of Li and White (10), the stability of the NaOI, as measured by the extent of I_2 consumption by soil organic matter or lignin, is shown to increase with increasing OH^- concentration and to decrease with increasing I^- concentration. An increase in I_2 strength had little effect upon the I_2 consumption by organic matter because the increase in the I^-/OH^- ratio so accelerates the rate of decomposition as to offset the increase in the initial concentration of NaOI (14).

If it is presumed that the increased I_2 consumption by the organic matter shown in figure 1 is due to increased stability of the NaOI, it must be concluded that the reagent used by Norman and Peevy (16) is of relatively low stability. Further, the reagent obviously gives results which fall on a steep part of the curve where a relatively small change in NaOH concentration will produce appreciable change in the stability of NaOI and hence in the consumption of I_2 by the organic matter. Because the reaction of NaOI with organic matter is never complete and only comparative measurements are being sought, an increase in the utilization of I_2 by soil organic matter brought about by a more stable NaOI reagent is not in itself desirable. It seems advisable, however, to increase the stability of the reagent so that minor changes in its composition will have minor effects

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[3] Supplied by the Mead Corporation, Chillicothe, Ohio.

[4] The reaction $3OI^- = IO_3^- + 2I^-$ is a second order reaction which obeys the rate law equation, $\frac{-d\,[OI^-]}{d\text{T}} = K[OI^-]^2$. Further, K is a function of the concentration of OH^- and I^- ions and equal to $2.9 + \frac{104[I^-]}{OH^-}$. Thus the stability of NaOI is shown to be increased by OH^- and decreasing I^- concentrations.

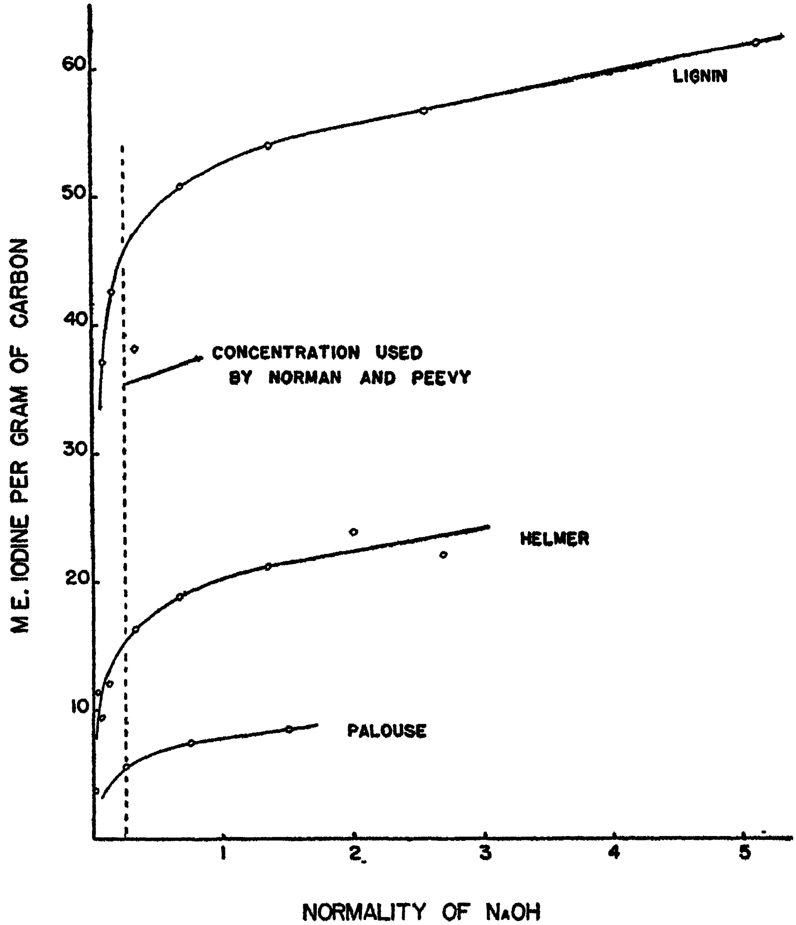

FIG. 1. EFFECT OF CONCENTRATION OF ALKALI UPON THE EXTENT OF IODINE CONSUMPTION BY ORGANIC MATTER

TABLE 4

Effect of I^- concentration upon the hypoiodite oxidation of lignin

FINAL CONCENTRATION OF		I_2 CONSUMED PER GRAM OF CARBON*
NaOH	KI	
N	*N*	*me.*
0.252	0.073	43.98
	0.116	42.66
0.754	0.073	49.29
	0.116	46.65

* Averages from duplicate titrations on duplicate samples.

upon the utilization of I_2 by organic matter. This change may be accomplished by increasing the concentration of NaOH from 1 to 3 N.[5] Although variation in I^- concentration produces only minor variations in NaOI stability, it is desirable to reduce the quantity to the minimum necessary for the reaction $I_2 + I^- = I_3^-$, which is approximately 20 gm. per liter, because the I^- concentration continually increases during the decomposition of NaOI and further accelerates the decomposition rate.

Effect of amount and condition of the soil

Absolute carbon content. Norman and Peevy (16) have indicated that the consumption of I_2 by organic matter depends on the weight of organic matter used. Data for eight soils, air-dried and ground to pass a 100-mesh sieve and of varying genetic origin and carbon content, and for lignin are reported in figure 2.

In all cases, the activity index of the soils falls as the weight of sample (carbon) increases, the rate of change being greater in the range of the larger samples. As the sample size increases, the rate of change in oxidation *tends* to approach zero. In all but one case (Spanaway), at least 100 per cent excess of I_2 was present. It seems difficult to explain these results simply on the basis of reduction in pressure of the oxidant. The substantially identical results with lignin indicate that physical interference from soil particles is not an important factor. The shapes of the curves differ: soils exhibiting a high reactivity (Rainier and Lynden) do not approach constant values, as do soils exhibiting low reactivity. The difference in shape and level of curves is believed to be indicative of chemical differences in the organic matter.

The data indicate conclusively that any comparison, to be valid, must be on the basis of equal weights of carbon, not on equal weights of sample. A sample weight yielding 0.10 gm. of carbon and characteristic of the area where the curves flatten would be preferable but not practical because the weight of sample for most soils would be excessively high, 7.5 gm. for soils containing 1.5 per cent carbon. A sample yielding 0.05 to 0.06 gm. of carbon is the most practical selection. Since the activity index, me. I_2 per gram of carbon, is the only valid basis for comparison, and since carbon analyses are essential, it is not inconvenient to employ a sample size such that a standard weight of carbon is taken.

Particle size and presoaking with NaOH. Accessibility of the organic matter to the hypoiodite reagent will undoubtedly affect the extent of oxidation; hence, the effect of fineness of grinding was investigated.

Four selected soils were ball-milled for arbitrary periods, and duplicate portions of each soil, each containing approximately 0.055 gm. of carbon, were subjected to hypoiodite oxidation. The data are reported in the first columns of table 5.

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[5] The stability of NaOI is indicated by the specific reaction rate of decomposition (in gram moles per liter per hour) according to the equation $3OI^- = IO_3^- + 2I^-$. When the concentration of NaOH is raised from 1 to 3 N, the specific reaction rate of decomposition falls from 34.3 to 13.3. As shown in figure 1, the nearly threefold increase in stability of the NaOI increases the I_2 consumption per gram of carbon for lignin from 46 and 52.5 me., for the Helmer soil from 15 to 19.5 me., and for the Palouse soil from 5.5 to 7.5 me.

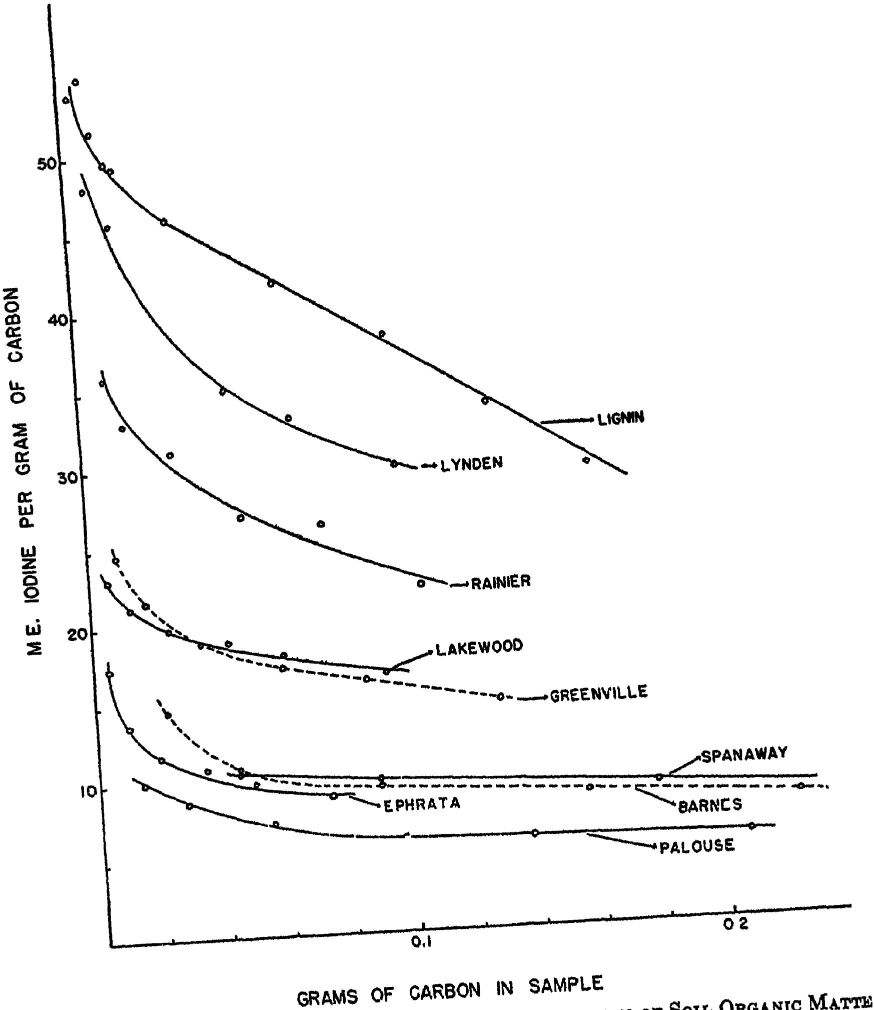

FIG. 2. EFFECT OF SAMPLE WEIGHT UPON IODINE CONSUMPTION OF SOIL ORGANIC MATTER AND LIGNIN

In all cases the unground material consumed less I_2 than the ground material. Grinding for more than 3 minutes, however, produced only small increases. Probably, the breakdown of aggregates to make them more accessible to the dispersing and solvent action of NaOH is desirable, but it is doubtful whether extremely fine grinding is necessary.

Since much of the soil organic matter is extractable in NaOH solution, the effect of addition of the NaOH some hours prior to addition of I_2 was investigated. The rate of dispersion of organic matter in NaOH depends on, among other things, the accessibility and condition of the organic matter and the time of contact and concentration of the NaOH. The effects of presoaking with NaOH were studied on four different soils by adding 25 ml. of 1 or 3 N NaOH 2.5 to 3 hours prior to addition of I_2. In general, the results obtained (14) indicate that presoaking with NaOH tends to increase the consumption of I_2 but that it has a diminishing effect as the fineness of grinding increases (table 5) or as the concentration of NaOH increases (table 6). The results indicate that presoaking

TABLE 5

Effect of fineness of grinding and presoaking with NaOH upon the activity index

SOIL	PERIOD OF BALL-MILLING	I_2 CONSUMED PER GRAM OF CARBON		
		Without presoaking	With presoaking*	Difference due to presoaking
	min.	*me.*	*me.*	*me.*
Palouse	0	4.62	5.35	+0.73
	3	5.64	6.31	+0.67
	7	5.59	5.97	+0.38
	15	5.65	5.68	+0.03
	30	5.46	5.55	+0.09
Helmer	0	8.80	11.09	+2.29
	3	15.28	20.83	+5.55
	30	16.21	21.41	+5.20
Ritzville	0	6.70	7.64	+0.94
	3	7.68	8.32	+0.64
	30	8.25	8.83	+0.58
Barnes	0	5.55	7.06	+1.51
	3	7.02	8.03	+1.01
	30	8.31	9.11	+0.80

* With 1N NaOH.

TABLE 6

Effect of presoaking with NaOH upon the activity index

SOIL	CONCENTRATION OF NaOH ADDED	PRESOAKING TREATMENT	I_2 USED PER GRAM OF CARBON	DIFFERENCE DUE TO PRESOAKING
	N		*me.*	
Palouse*	1	−	5.65	
		+	5.97	+0.35
	3	−	7.45	
		+	7.47	+0.02
Helmer†	1	−	16.20	
		+	21.40	+5.20
	3	−	21.35	
		+	21.40	+0.05

* Ball-milled for 7 minutes.

† Ball-milled for 30 minutes.

has one or both of two functions: it may, and undoubtedly does, increase dispersion of aggregates, and it has a more extensive dispersive and solvent action upon the organic matter. Where the initial dispersion is adequate, NaOH can extract the organic matter in a period of minutes. An increase in NaOH strength has qualitatively the same effect. The possibility also exists that presoaking brings about an alteration of the organic matter (such as cleavage of carbohydrates), making it more susceptible to oxidation. Presoaking was observed (14) to decrease I_2 consumption in one soil (the B horizon of Alderwood) ground to pass a 100-mesh sieve. The reversal of effect of presoaking in this one case cannot be explained with the information at hand. The diminishing tendency of presoaking with NaOH to increase the consumption of I_2 with decreased particle size suggests that the extraction of organic matter is an essential part of the hypoiodite oxidation process.

TABLE 7

Volume error resulting from titration of suspensions

SAMPLE AND TREATMENT	$Na_2S_2O_3$ USED PER 10 ML. ALIQUOT*
	ml.
Blank	16.360
Blank + 1% bentonite	
Supernatant liquid	16.353
1.43% suspension	16.203

* Average of three.

TABLE 8

Effect, upon the activity index, of dilution of soil with bentonite

SOIL	TREATMENT		I_2 USED PER GRAM OF CARBON	DIFFERENCE DUE TO BENTONITE
			me.	*me.*
Alderwood	No presoaking with NaOH	No bentonite	19.37	
		1% bentonite	18.22	1.15
	Presoaked	No bentonite	18.96	
		1% bentonite	17.89	1.07
Barnes	No presoaking	No bentonite	8.37	
		1% bentonite	7.95	0.42

Dilution with bentonite. The effect of dilution of soil with a material neutral to NaOI was investigated by adding 1-gm. portions 200-mesh bentonite[6] to two soils and comparable blanks. Although the bentonite slaked poorly in water, it slaked readily in 0.5 *N* NaOH, settling out rapidly and carrying down suspended soil material. A perfectly clear supernatant liquid which was easily sampled and titrated resulted.

Some measure of the volume error introduced by titration of soil suspensions is given by the data in table 7 on the titration of blanks containing bentonite only. Bentonite itself consumes no I_2 (14). The titration of bentonite suspension is analogous to the titration of soil suspensions. Since there are no compensatory volume errors in the usual blanks, titration of aliquots containing soil will introduce a negative error which will result in a figure that will indicate a higher consumption of I_2 than actual.

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[6] Volclay of the American Colloid Co., Chicago, Illinois.

The data on the soil-bentonite systems (table 8) indicate that dilution of the soil with bentonite reduces the usage of I_2 by the soil. Since supernatant liquid was sampled for titration, volume errors are not responsible, and no clue is available in the data to explain this reduction. Simple dilution and mechanical interference or formation of shielding complexes may be responsible.

Discussion

The results from the study of the effect of the condition of the soil upon the value of the activity index are instructive but inconclusive. It is recommended, however, that the soil be crushed prior to oxidation to destroy all but the smallest of aggregates without crushing primary soil particles. The conflicting data on the effect of presoaking with NaOH do not warrant any definite recommendation. The decrease in the activity index of the Alderwood B horizon resulting from presoaking may be characteristic of the Alderwood soil or of B horizon material. No data are available to support any further conclusion.[7] Further work on this phase is necessary. The depressing effect upon the activity index of dilution of the soil with bentonite also requires additional study.

SUMMARY AND CONCLUSIONS

The general suitability of NaOI and the hypoiodite method proposed by Norman and Peevy as a tool for studying the nature of organic matter is reviewed, as are the probable reactions of NaOI with organic matter.

The chemistry of the pretreatment of soils with HCl-KI solution is reviewed and experimental work is presented to warrant the following conclusions:

1. The inorganic oxidants commonly found in soils (Fe^{+++} and MnO_2) do not oxidize I^- to I_2 in alkaline medium.
2. Pretreatment induces the formation of reductants which reduce I_2 to I^-.
3. Substitution of H_3PO_4 for HCl in pretreatment will largely prevent the solution and reduction of Fe^{+++} but does not eliminate the interference due to Fe^{++} or to Mn^{++}.
4. Without regard to the question of removal of possible peroxides or organic oxidants, it seems advisable to abandon pretreatment in its present form, since it introduces Fe^{++} and Mn^{++}, which reduce I_2 in alkaline solution, and thus leads to erroneous results.
5. Use of aliquots of the supernatant liquid and acidification with H_3PO_4 rather than with HCl improve the end point and minimize possible error resulting from the solution of MnO_2 or Fe^{+++} during the titration phase of the hypoiodite procedure.

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[7] Presoaking with NaOH involves problems that cannot be considered here. Mattson (The oxidation-reduction condition in vegetation, litter and humus: I. *Ann. Agr. Col. Sweden* 11: 135–144, 1943) has shown that suspensions of organic materials in alkaline solutions can absorb large quantities of atmospheric O_2. In this process the organic matter is extensively oxidized.

A study of the effect of varying concentrations of the basic hypoiodite reagents, I_2, I^-, and NaOH, shows that the variation in the activity index, milliequivalents I_2 per gram of carbon, parallels the variation in stability of the active reagent, NaOI. The consumption of I_2 by soils and lignin is increased by increasing the concentration of OH^- and depressed by concentrations of I^-.

The absolute carbon content of the system has an appreciable effect upon the activity index. Small samples react more extensively with hypoiodite than do large samples. Materials of high reactivity exhibit steeper curves for plots of milliequivalents I_2 per gram of carbon versus total weight of carbon than do materials of low reactivity. Strict comparison is valid only on the basis of equivalent amounts of carbon. Grinding of soils or presoaking with NaOH several hours prior to hypoiodite oxidation leads to an increase in the activity index. Extraction of the organic matter in NaOH appears to be an essential for maximum reaction of hypoiodite and organic matter. Dilution of the soil with an inert material such as bentonite reduces the activity index for reasons not yet apparent.

It may be concluded from this study of the conditions affecting the extent of reaction of hypoiodite with soil organic matter and lignin that the consumption of I_2, expressed as milliequivalents I_2 per gram of carbon and termed the "activity index," depends upon three principal factors: 1. Composition of the oxidizing medium; 2. Absolute amount of carbon in the system; 3. Physical condition of the sample.

On the basis of this study, it seems advisable to modify the procedure of Norman and Peevy to remove it as far as possible from critical regions characteristic of it. The sample size should be so chosen that comparisons can be made between equal weights of carbon. A weight of 0.055 gm. of carbon is suggested. The concentration of NaOH should be raised from 1 *N* to 3 *N* and the KI concentration lowered to a minimum, 20 gm. per liter. The resultant increase in stability of the hypoiodite will increase the consumption of I_2 and reduce to a minimum the factors of physical interference. Acidification with H_3PO_4 and sampling of the supernatant liquid will reduce errors in the titration phase of the procedure. Because of the increased stability of the hypoiodite, the reaction time should be increased from 1 to 1.5 hours. A detailed procedure embodying these recommendations follows:

Soil samples should be crushed to break down all but the finest of aggregates before they are subjected to hypoiodite oxidation. Calculate the sample size required to contain 55 mgm. of carbon, and weigh with an accuracy of 1 mgm. a sample within ± 10 mgm. of the desired weight of soil. Transfer quantitatively to a 125-ml. Erlenmeyer flask,[8] and add, with constant shaking, 25 ml of distilled water, 25 ml. of 3 *N* NaOH, and 50 ml. of 0.1 *N* I_2 (12.7 gm. of I_2 and 20.0 ± 0.1 gm. of KI per liter). Stopper tightly with a rubber stopper which has been cleaned by boiling in dilute NaOH, shake at 3- to 5-minute intervals for 25 to 30 minutes, and set aside in the dark for 1 hour. Set up a blank under identical conditions, omitting the sample. Pipette triplicate 10-ml. aliquots into 50- to 60-ml. portions of distilled water in 250-ml. Erlenmeyer flasks. Disturb the suspension as little as possible and take only supernatant liquid. Small volume errors result from varying density of suspension. Acidify the aliquots with 5 ml. of 6 N H_3PO_4, and titrate the liberated I_2 with 0.03 N $Na_2S_2O_3$ from a 25-ml. burette. When the color becomes a faint yellow, add 5 ml. of 0.2 per cent starch solution and complete the titration, rinsing down the sides of the flask with a few milliliters of water within a few drops of the end point. Since many soils yield yellow-colored solutions, the starch may have to be added as much as 1 ml. in advance of the endpoint on the first titration. Subtract the average of the three titrations from the value for the blank to find the milliliters of $Na_2S_2O_3$ equivalent to the I_2 used by the sample. Where duplicate samples are used, duplicate titrations are adequate, provided duplicates check with 0.05 ml. for each sample, and the averages check within 0.1 ml. between samples.

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[8] Values obtained with flasks stoppered with rubber that has been cleaned by boiling for 30 minutes with dilute NaOH solution are not detectably different from those obtained with glass-stoppered flasks.

$$\text{me. } I_2 \text{ per gram of carbon} = \frac{\text{ml. } Na_2S_2O_3 \times N \text{ of } Na_2S_2O_3 \times 10 \times 100}{\text{wt. of sample} \times \text{per cent carbon in sample}}$$

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This report was compiled under the supervision of the Soil Conservation Service of the U. S. Department of Agriculture, with the cooperation of the Forest Service, Army Corp of Engineers, Coast and Geodetic Survey, Bureau of Reclamation, Geological Survey, Office of Land Utilization, Federal Power Commission, and Tennessee Valley Authority. It is intended to cover all the known publications in English on the engineering aspects of sedimentation. A shelf-by-shelf canvass was made of all engineering and geological literature in the principal libraries in New York City and of the proceedings and transactions of 150 of the leading engineering societies of the world. Nearly 100,000 separate issues of journals, books, and reports published prior to 1942 were reviewed, and a fairly complete canvass was made of later literature on this subject. A tremendous amount of work has gone into the preparation of the material for this bulletin. It should be readily available to everyone concerned with this problem.

Conservation of Natural Resources. Edited by GUY-HAROLD SMITH. John Wiley and Sons, Inc., New York, 1950. Pp. 552. Price $6.

Twenty specialists in the various phases of conservation contributed to the preparation of the material for this book. They deal with the history of the conservation movement, soil and crop resources, forests, water, minerals, wildlife, recreational facilities, and conservation planning. The book is essentially a revision of an earlier volume, "Our Natural Resources and Their Conservation," which first appeared in 1936. The tabular material has been brought up to date and there is considerable evidence of advancement in the thinking of the authors in comparison with that of the earlier contributors. The authors have rendered a very important service in bringing together in one volume a mass of data on our several natural resources and in providing some thought-provoking discussions concerning them. The book has high value for reference purposes.

Irrigation Principles and Practices. Second Edition. By ORSON W. ISRAELSEN. John Wiley and Sons, Inc., New York, 1950. Pp. 405, figs. 180. Price $6.

The author, by reason of his wide experience in consulting work on ground water development, construction of storage reservoirs, drainage, and flood control, is especially well qualified to deal with the principles and practices of irrigation in arid areas. The book shows abundant evidence of exact knowledge on the subject. Its 18 chapters cover all phases of the problem. They include one chapter on irrigation in humid climates and another on social and administrative aspects of irrigation. The appendixes contain more than 150 problems, with answers, for class purposes, and some 300 references, arranged by chapters. The illustrations are excellent. Everyone who has to do with practice or research in irrigation will find this a very useful volume to have at hand.

Moisture Requirements in Agriculture. By HARRY BURGESS ROE. McGraw-Hill Book Company, Inc., 1950. Pp. 413, figs. 150. Price $5.50.

The author of this book has rendered a highly important service in assembling the available material on soil moisture, with special reference to farm irrigation. The first few chapters deal with soil moisture relations, plant requirements, sources of water, its flow and measurement, and interrelations between irrigation and drainage. The remaining chapters present the principles of irrigation, time of irrigation, use of water, methods, structures, pumping, irrigation of specific crops, irrigation farming and legislative problems, with a final chapter on supplemental irrigation in humid regions. The appendix contains 153 references, on which the author comments in the text, and 60 additional references that were consulted. The material is well presented, and the illustrations are excellent. The book is entitled to a wide reading on the part of both those who do research work in irrigation and those who put it into practice.

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